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The Synthesis of 1,4-bis(2-(4-(4-fluorobenzoyl)phenoxyethoxy)Benzene and poly(aralkyl ether)s Derived from 1,4-bis(2-tosyloxyethoxy)Benzene

Juraj Drzic
Wright State University

THE SYNTHESIS OF 1,4-BIS(2-(4-(4-FLUOROBENZOYL)PHENOXYETHOXY)BENZENE AND POLY(ARALKYL ETHER)S DERIVED FROM 1,4-BIS(2-TOSYLOXYETHOXY)BENZENE

A thesis submitted in partial fulfillment
of the requirements for the degree of
Master of Science

By

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B.S., University of Zagreb, Faculty of Chemical Engineering and Technology, 2012

2014
Wright State University

WRIGHT STATE UNIVERSITY

GRADUATE SCHOOL

May 29, 2014

I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY Juraj Drzic ENTITLED The Synthesis of 1,4-Bis(2-(4-(4-fluorobenzoyl)phenoxyethoxy)benzene and Poly(aralkyl ether)s Derived from 1,4-Bis(2-tosyloxyethoxy)benzene BE ACCEPTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF Master of Science .

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ABSTRACT

Drzic, Juraj M.S., Department of Chemistry, Wright State University, 2013. The Synthesis of 1,4-Bis(2-(4-(4-fluorobenzoyl)phenoxyethoxy)benzene and Poly(aralkyl ether)s Derived from 1,4-Bis(2-tosyloxyethoxy)benzene.

The reaction of 1,4-bis(2-tosyloxyethoxy)benzene or 1,4-bis(bromoethoxy)-benzene with 4-fluoro-4'-hydroxybenzophenone was carried out under a variety of conditions. Changes were made in solvent, reaction time, work-up and base. All attempts to generate a bis(fluorobenzophenone) monomer were unsuccessful. In some cases the presence of the half-product could be determined. In other cases, an elimination product was indicated. The ditosylate, 1,4-bis(2-tosyloxyethoxy)benzene was reacted with bisphenol-A, bisphenol-AF, bis(4-hydroxyphenyl)diphenylmethane and 9,9-bis(4-hydroxyphenyl)fluorene in a dioxane - water solution in the presence of sodium hydroxide to produce four polymers. The polymers were characterized by thermal analysis (TGA) to reveal 5% weight loss temperatures of 338°, 350°, 365° and 377°, respectively. The increase in thermal stability, as judged by the 5% weight loss values, appears to be related to the aromatic content. The polymers exhibited reasonable solubility in a variety of solvents.

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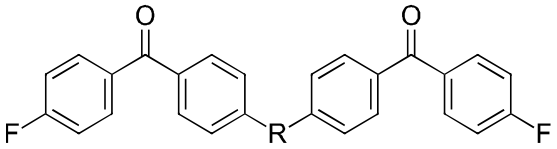
I would also like to acknowledge the faculty, staff, and graduate students of the Wright State Chemistry Department for all I have learned from them.

DEDICATION

To my advisor Dr. William A. Feld for his guidance and many useful advices during my stay in the USA; to my friends and colleagues at Wright State University and friends from all over the world, for their support and tireless company and good times, to my parents who helped me to get where I am now.

INTRODUCTION

Poly(arylene ether)s (PAE) and poly(ether ether ketone)s (PEEK) are important classes of high performance thermoplastics and offer a combination of excellent chemical, physical and mechanical properties. They find application as coatings, adhesives and structural resins for aerospace vehicles and related systems.



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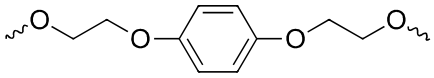


2

Bis(fluorobenzophenone) monomers **1**, containing different center groups, like poly(oxyalkylene) groups (some containing tertiary amine functions) can be used to synthesize PEEKs with various bisphenol comonomers. Inserting a hydroquinone unit as a center group as illustrated in **2** by using 1,4-bis(2-tosyloxyethoxy)benzene is expected to increase the rigidity and T_g of the polymer.

The objective of this research was to investigate the use of 1,4-bis(2-tosyloxy-ethoxy)benzene in 1) the synthesis of a new bis(fluorobenzoyl) monomer containing a hydroquinone/oxyalkylene hybrid subunit and 2) the synthesis of a series of polyethers employing bisphenol-A and related "kinked" bisphenols followed by characterization.

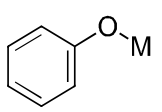
HISTORICAL

Poly(ether ether ketone)s (PEEK) possess good properties which make them useful as engineering thermoplastics. They have good resistance to strong chemicals and semicrystaline PEEKs have good thermal stability with melting points up to 400°. They are however, hard to process because of their high melt transitions. On the other hand, amorphous PEEKs have better processability due to their lower glass transitions and higher solubility but these properties also lower their possible applications.[1]

The most common way of synthesizing PEEKs is a nucleophilic substitution of activated aromatic dihalides with bisphenolates. Many bisphenolates are commercially available and activated aromatic dihalides have been prepared by Friedel-Crafts acylation as well as several other reaction sequences.

Nucleophilic aromatic substitutions

Aryl ethers **5**, synthesized by Bunnett and Zahler in 1951,[2] show that it is possible to react alkali metal phenolates **3** with aromatic halides **4** possessing electron-withdrawing groups either *ortho* or *para* to the halogen which is being displaced.



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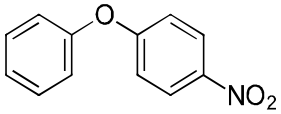
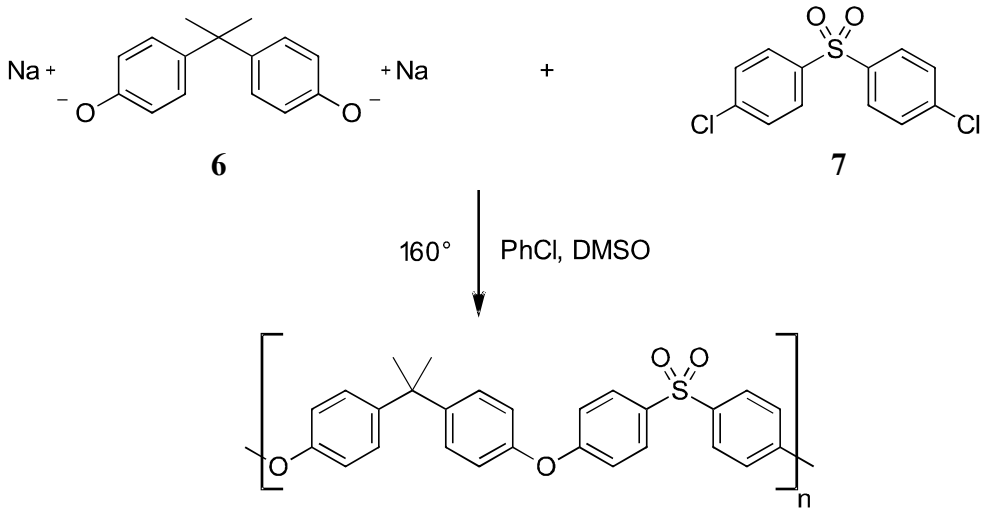


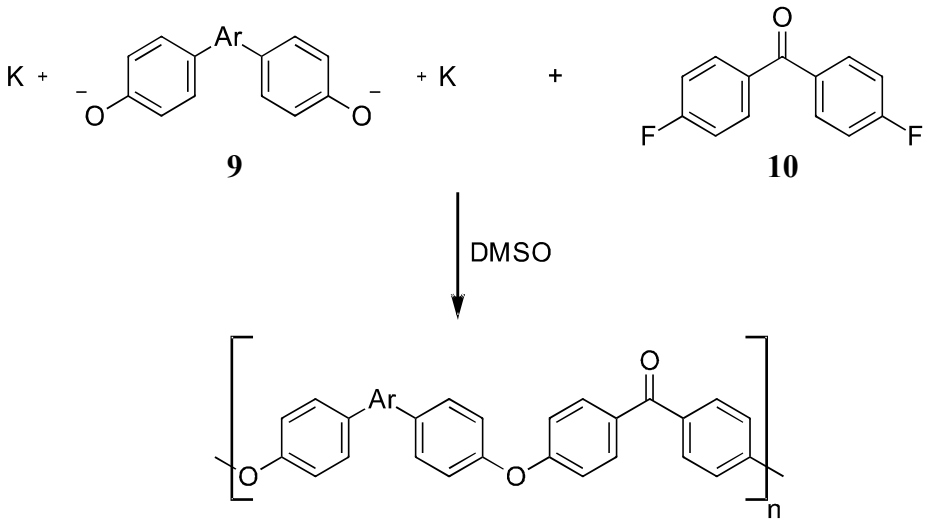
5

In 1967, using similar methods, Johnson et al.[3] synthesized a poly(ether sulfone) **8** by the reaction of the sodium salt of bisphenol-A **6** and bis(p-chlorophenyl) sulfone **7** in a chlorobenzene/DMSO solvent mixture at 160°C under a nitrogen atmosphere.



6 **7** **8**

In 1972, Vinogradova et. al.[4] synthesized aromatic polyethers **11** using bisphenolates **9** in a reaction with 4,4-difluorobenzophenone **10** in DMSO at elevated temperatures.

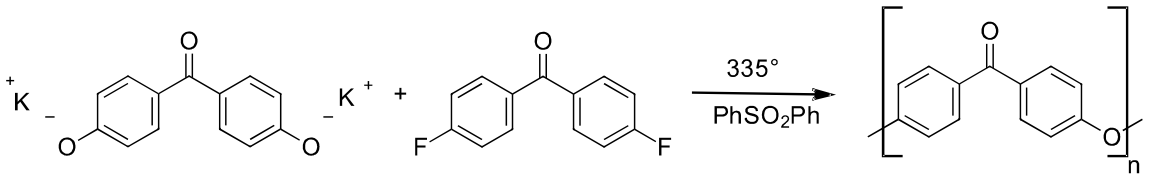


9 **10**

11

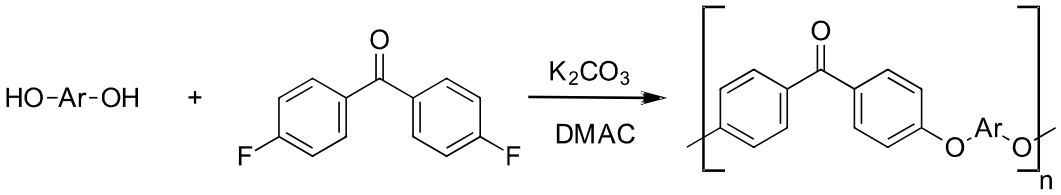
Ar = aromatic groups

The synthetic method for making PEEK **13,** which is used commercially today, was developed in 1981 by Attwood et. al.[5]. The bispotassium salt of bis(4-hydroxy-phenyl)ketone **12** was reacted with **10** in diphenyl sulfone at 335° for 2-3 hours.



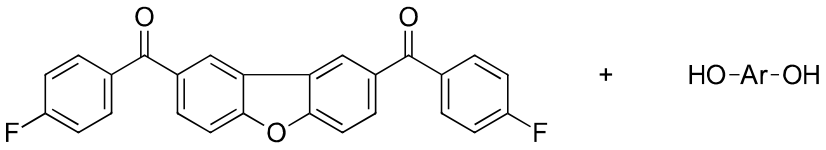
12 **10** **13**

The same method was utilized by Hergenrother et.al. in 1988[1] to make a series of poly(ether ketone)s **15**. Instead of diphenyl sulfone, a dimethylacetamide (DMAC)/K_2CO_3 solution was used as a solvent system for the reaction of **10** with dihydroxyaryl compounds **14**. Some of these polymers were reported to have viscosities as high as 1.9.

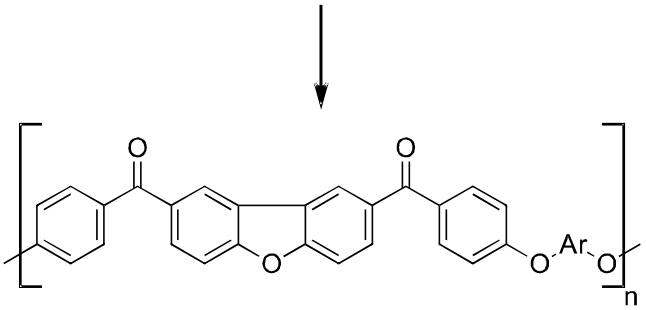


14 **15**

In last two decades, attention has been focused on obtaining poly(ether ether ketone)s from different dihalide monomers like the difluorodibenzofuran monomer **16** which can be reacted with various bisphenols **14**. In 1991, a similar idea was utilized and poly(arylene ether ketone)s **17** were synthesized by Cormier et.al.[6]

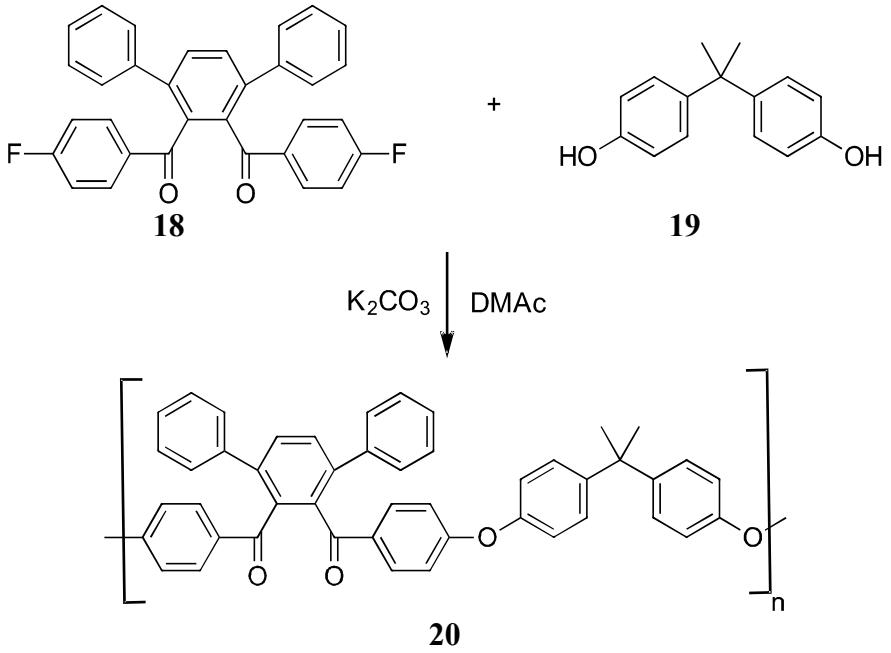


16 **14**



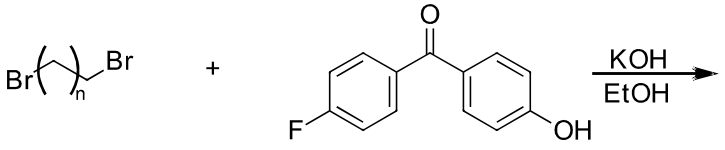
17

High-molecular-weight polymers **20** were prepared by Singh and Hay[7] by reacting the novel fluoro monomer **18** with bisphenol-A **19**. The polymers had good solubility in common organic solvents and they formed flexible, colorless and transparent films.

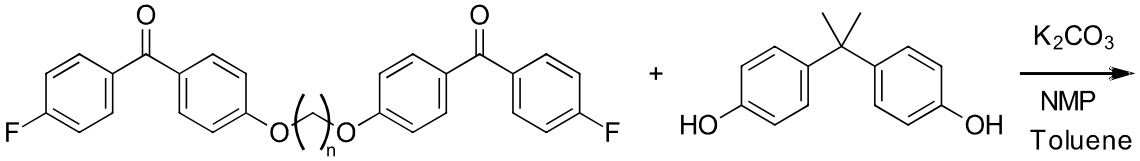


18 **19** **20**

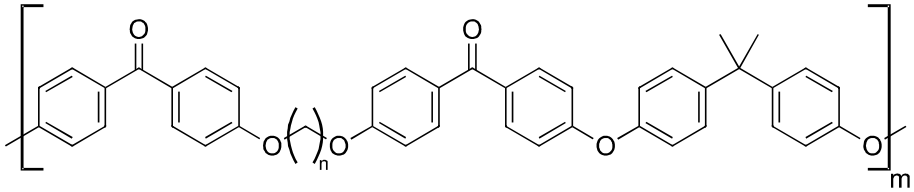
In 1992, B. Patel[8] reported the synthesis of poly(ether ether ketone)s **24a-e** containing alkane chains of different length. Bis(fluorobenzophenone) monomers **23a-e** used in polymerizations were synthesized by a nucleophilic substitution reaction of 4-fluoro-4'-hydroxybenzophenone **22** with various dibromoalkanes **21a-e**. These monomers were used in a condensation polymerization with **19** in NMP/toluene using potassium carbonate as the base. The polymers could be cast into flexible, colorless and transparent films and their T_gs were inversely proportional to the length of the alkene chain in the monomer unit. The thermal stability of these polymers was good with a 5% weight loss at 450° in both air and nitrogen.



21a - e, n = 1 – 5 **22**



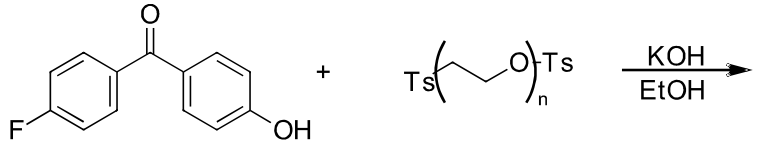
23a - e, n = 1 – 5 **19**



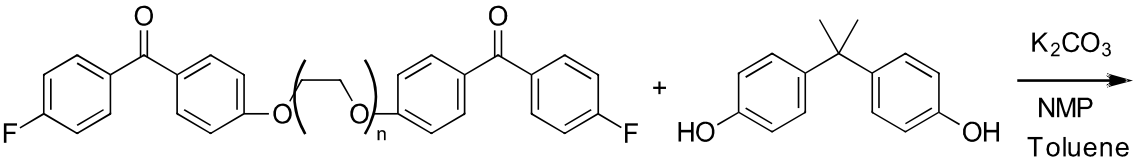
24a – e, n = 1 - 5

A similar synthetic sequence was reported the same year by M. Patel.[9] Poly(ether ether ketone)s with multiple oxyalkylene units **27a-d** were synthesized.

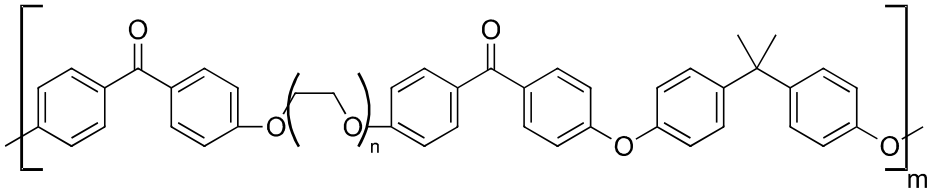
Bis(fluorobenzophenone) monomers **26a-d** were synthesized from **22** with different



22 **25a - d**, n = 1 - 4



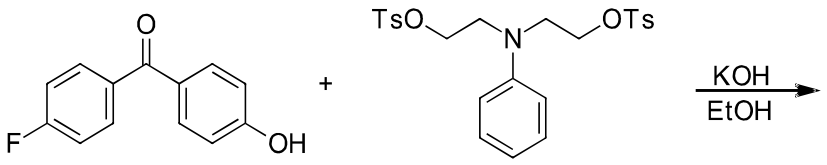
26a - d, n = 1 – 4 **19**



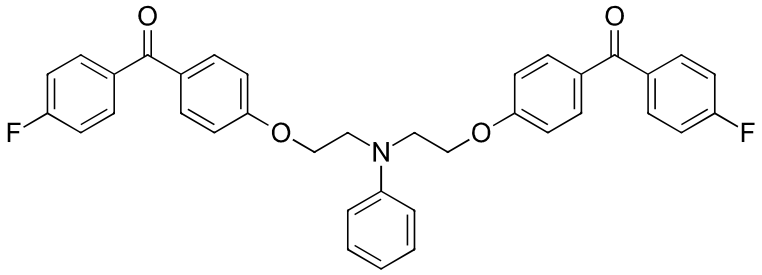
27a - d, n = 1 - 4

ethylene glycol ditosylates **25a-d** in ethanol by nucleophilic substitution in the presence of potassium hydroxide. The condensation polymerization of the described monomers was carried out in NMP/toluene using potassium carbonate as a base with **19**. These polymers had good thermal stability with 5% loss in weight at 450°C in both air and nitrogen. Flexible transparent films were obtained.

In 2004. McGinty synthesized two different poly(ether ether ketone)s in a similar way as for the previous two examples. The new polymers contained a tertiary amine subunit. The ditosylate **28** with tertiary amine subunit was reacted with **22** in the presence of potassium hydroxide in ethanol to synthesize the bis(fluorobenzophenone) monomer **29**.

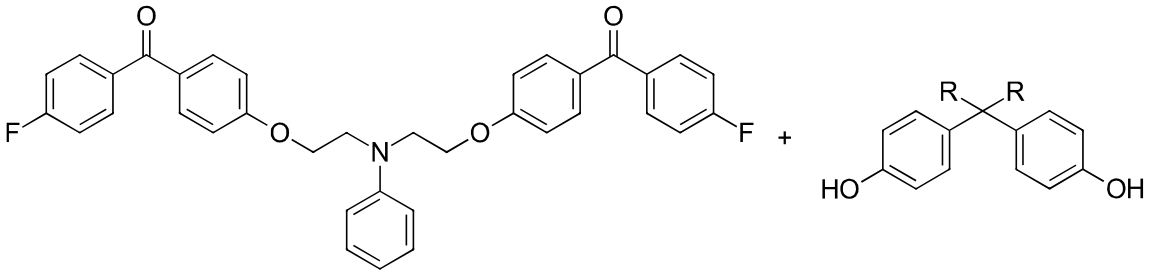


22 **28**

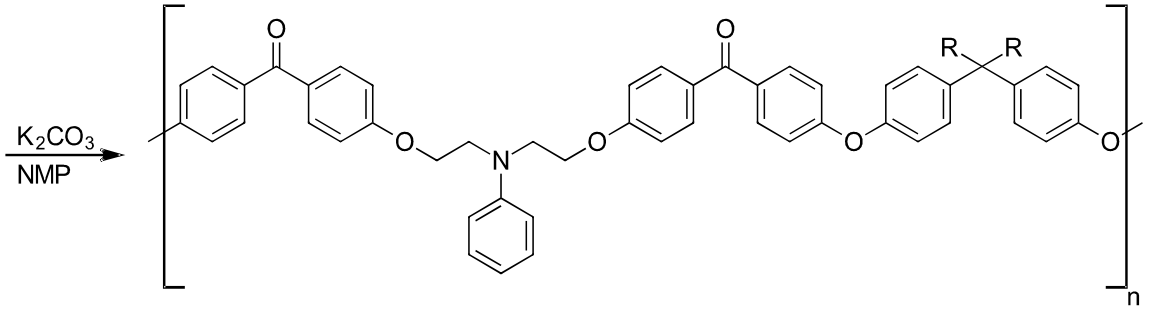


29

Polymerization of **29** was carried out in NMP using potassium carbonate as a base and toluene as dehydrating agent with an appropriate bisphenol. Bisphenol-AF **30** as well as the bisphenol-A **19** were used in the polymerization to yield the corresponding poly(ether ether ketone)s **31a - b**.

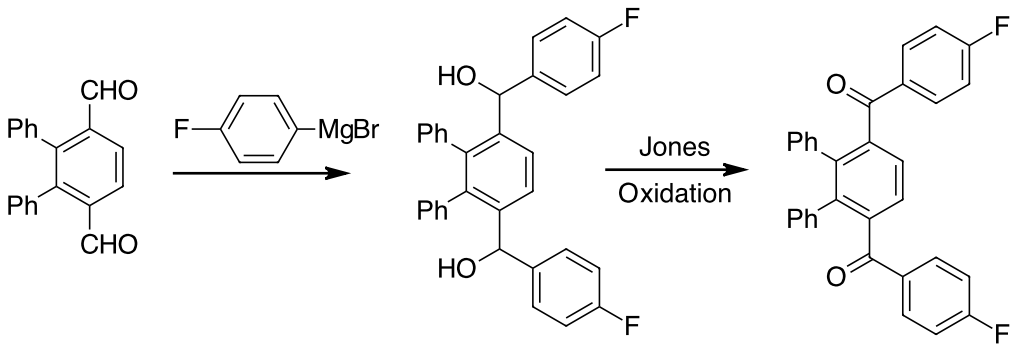


29 **19**, R = CH_3, **30,** R = CF_3



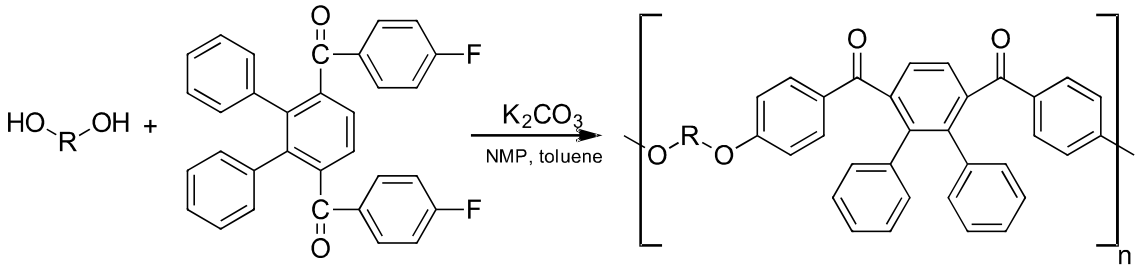
31a, R = CH_3, **31b**, R = CF_3

Another example of preparing poly(ether ether ketone)s with bis(fluorobenzoyl) monomer **34** was reported by Dancevic in 2005.[10] Preparation of **34** was accomplished by reacting the dialdehyde **32** with a Grignard reaction prepared with the p-bromofluoro-benzene in THF. The second step of preparing **34** involved the Jones oxidation of the intermediate diol **33** obtained in the first step.

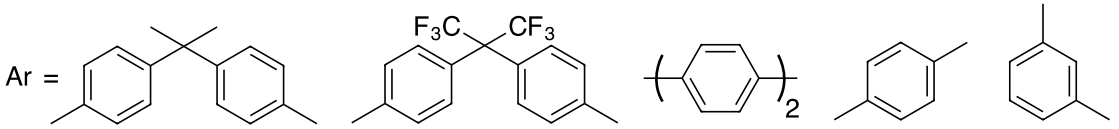


32 **33** **34**

Polymerization of **34** was carried out with various bis(hydroxyl compounds) **35a-e** in NMP using potassium carbonate as base and toluene as dehydrating agent yielding polymers **36a-e** shown below.



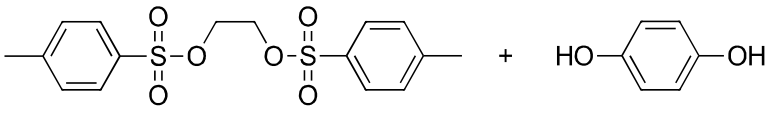
35 **34** **36a - e**



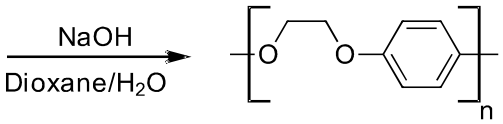
35a, 36a **35b, 36b** **35c, 36c** **35d, 36d** **35e, 36e**

Tosylate Group Substitutions by Phenols

In 1950 patent, Reeder and Wallsgrove[11] reported production of linear polymers by reacting different diphenols with various disulphonic esters. The solvent system used for the reactions was a mixture of dioxane and water with sodium hydroxide as base. One example is the reaction of ethylene di(p-toluenesulfonate) **37** and hydroquinone **38**. The product, polyether **39,** was white powder melting in a temperature range of 240° to 270°.

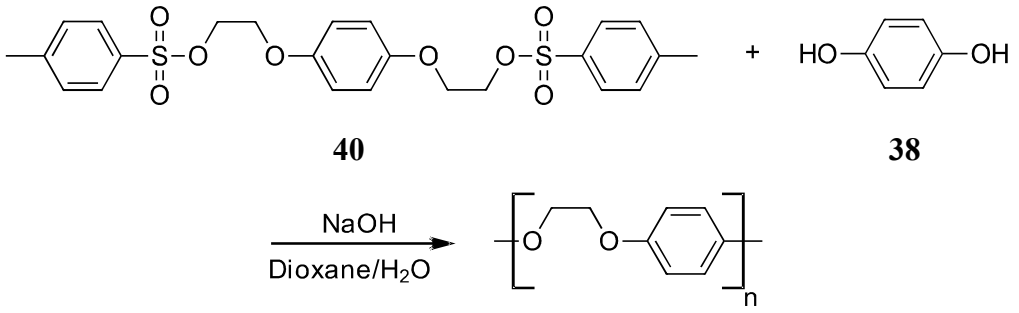


37 **38**



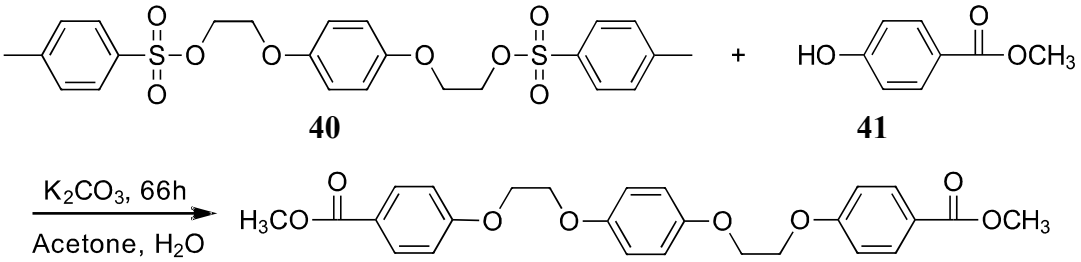
39

Alternately, the reaction of 1,4-bis(2-tosyloxyethoxy)benzene **40** with **38** yields a product with the same repeating unit as **39**.



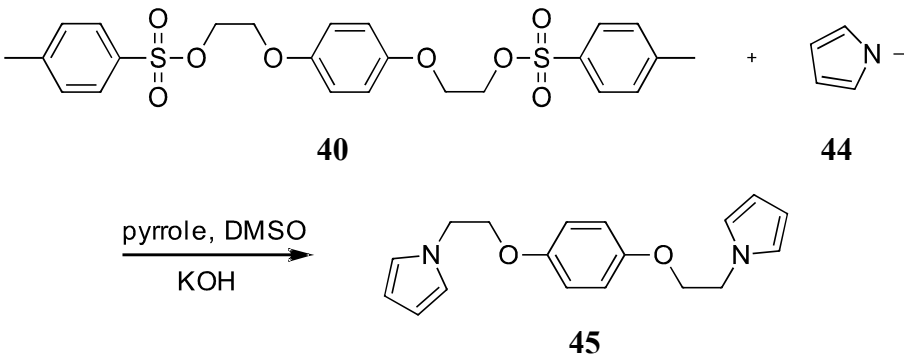
40 **38** **39**

In 1966, Jones and Mather[12] prepared a series of fiber forming polyesters. The reaction of methyl p-hydroxybenzoate **41** with the ditosylate **40** yields 1,4-bis(2-(4-methoxycarbonylphenoxy)ethoxy)benzene **42** which was used in the preparation of polyesters.



40 **41** **42**

In 2003, Ono et al.[14] reported the synthesis of materials used for the electrochemical synthesis of polymers with crosslinked structures. The reaction of



40 **44** **45**

ditosylate **40** with the pyrrole **44** yields 1,4-bis(2-(N-pyrrolyl)ethoxy)benzene **45**. It was electrochemicaly polymerized to produce uniform thin films that could be doped to produce conductive films.

The successful nucleophilic substitution of the tosyl functions in **40** suggests that reactions analogous to those reported by Patel, Patel and McGinty could be extended to **40**. Thus, the main objective of the current research was the study of the reaction of **40** with 4-fluoro-4'-hydroxybenzophenone **22** to provide monomers similar to **23a-e**, **26a-d** and **29** that could be used in polymerization reactions with diphenols under typical PEEK synthesis conditions.

Experimental

Instrumentation and Chemicals

Melting points were obtained with a DigiMelt MPA-160 or Electrothermal MP Apparatus. Nuclear magnetic resonance (NMR) ^{1}H and ^{13}C spectra were obtained using a Bruker Avance 300 MHz NMR Spectrometer. Solvents for NMR were $CDCl_3$, DMSO-d_6, and Acetone-d_6. Thermal Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) spectra were obtained with a TA TGA Q 500 and a TA DSC Q 200 both employing a N_2 atmosphere. Infrared (IR) spectra were recorded as thin films (KBr) with a Nicolet 6700 FT-IR spectrometer. Chemicals were purchased from Aldrich and used as received.

1,4-bis(2-tosyloxyethoxy)benzene, 40

Into a 250 mL, round-bottomed flask equipped with a magnetic stirrer and an addition funnel containing a solution of 1,4-bis(2-hydroxyethoxy)benzene (6 g, 30 mmol) in THF(90 mL) was added an aqueous sodium hydroxide solution (7 g in 20 mL, 175 mmol) and the mixture was cooled to 0˚. A solution of tosyl chloride (12.4 g, 65 mmol) in THF (35 mL) was added dropwise and the solution was stirred for 2 h at 0˚. The reaction mixture was poured into water (200 mL), stirred overnight, filtered and dried to yield a white precipitate (14.5 g, 93%): mp 144° - 149°; ^{1}H NMR ($CDCl_3$) δ 2.46 (s, 6H, CH_3), 4.10 (t, 4H, -CH_2-), 4.35 (t, 4H, -CH_2-), 6.71 (s, 4H, Ar hydroquinone), 7.34 (d, 2H, Ar tosyl), 7.83 (d, 2H, Ar tosyl).

1,4-Bis(bromoethoxy)benzene, 48

A solution of 1,4-bis(2-hydroxyethoxy)benzene (5.000 g, 0.0250 mol) and triphenylphosphine (15.801 g, 60 mmol) in acetonitrile (38 mL) was prepared in a 100 mL, round-bottomed flask equipped with an addition funnel and a magnetic stirrer. The solution was cooled with an ice bath and tetrabromomethane (20 g, 60 mmol) was slowly added with vigorous stirring. The reaction mixture was stirred at rt for 4 h and cold water (30 mL) was added to form a white precipitate. The precipitate was collected and washed with a methanol/water mixture (3/2, 3x15 mL). The product was recrystallized from methanol (10 mL) to yield 3.5 g of white crystals (43%): mp 112° -116°; ^{1}H NMR ($CDCl_3$) δ 3.63 (t, 4H, CH_2), 4.26 (t, 4H, CH_2), 6.88 (s, 4H, aromatic).

Fluorobenzophenone monomer, 49

The synthesis of a bis(fluorobenzophenone) monomer from ditosylate **40** and 4-fluoro-4'-hydroxybenzophenone **22** was carried out using several combinations of solvent, reactant ratios and reaction times.

Fluorobenzophenone monomer – 1st attempt

In a 100 mL, round-bottomed flask equipped with a condenser, drying tube and a magnetic stirrer was placed a solution of KOH (88.7%) pellets (0.33 g, 6 mmol) in EtOH (18 mL), 4-fluoro-4'-hydroxybenzophenone **22** (1.3 g, 6 mmol) and 1,4-bis(2-tosyloxyethoxy)benzene **40** (1.0 g, 1.9 mol). The reaction mixture was refluxed for 18 h, cooled, and poured into water (180 mL). The mixture was stirred, filtered and dried to yield a white precipitate (1.102 g, 97%): mp 217° - 225°.

Fluorobenzophenone monomer – 2nd attempt

In a 100 mL round-bottomed flask equipped with a condenser, drying tube and a magnetic stirrer was placed a solution of KOH (88.7%) pellets (1.340 g, 24 mmol) in EtOH (80 mL) and 4-fluoro-4'-hydroxybenzophenone **22** (5.202 g, 24 mmol) was added. Then reaction mixture was heated to 40° and 1,4-bis(2-tosyloxyethoxy)benzene **40** (3.800 g, 7.6 mmol) was added. The reaction mixture was refluxed for 20 h, cooled and poured into water (400 mL). The mixture was filtered and dried to collect a white-yellow precipitate (4.301 g, 95%).

Fluorobenzophenone monomer – 3rd attempt

In a 50 mL, round-bottomed flask equipped with a condenser, drying tube and a magnetic stirrer was placed a solution of K_2CO_3 (0.572 g, 4.1 mmol) in NMP (12 mL), 4-fluoro-4'-hydroxybenzophenone **22** (0.894 g, 4.1 mol) and 1,4-bis(2-tosyloxyethoxy)benzene **40** (1.000 g, 1.97 mmol). The reaction mixture was stirred at 90° for 6 h, cooled and poured into 200 mL of a saturated sodium bicarbonate solution. The mixture was stirred overnight, filtered and dried to yield a white-yellow precipitate (0.884 g, 75%).

Fluorobenzophenone monomer – 4th attempt

In a 50 mL, round-bottomed flask equipped with a nitrogen inlet, a condenser and a nitrogen outlet, drying tube and a magnetic stirrer was placed K_2CO_3 (0.925 g, 6.7 mmol) dissolved in an acetone/water mixture (6.5/3.5, 20 mL) followed by the addition of 4-fluoro-4'-hydroxybenzophenone **22** (1.405 g, 6.5 mmol) and 1,4-bis(2-tosyloxyethoxy)benzene **40** (1.500 g, 2.9 mol). The reaction mixture was refluxed for 66

h, cooled and poured into 50 mL of water. The precipitate was slurried with hot methanol (12 mL), filtered and dried to give a white precipitate (1.471 g, 85%).

Fluorobenzophenone monomer – 5th attempt

In a 50 mL, round-bottomed flask equipped with a nitrogen inlet, a condenser and a nitrogen outlet, drying tube and a magnetic stirrer was placed NaOH (0.523 g, 13.0 mmol) dissolved in a dioxane/water mixture (5/4, 18 mL) followed by the addition of 4-fluoro-4'-hydroxybenzophenone **22** (1.401 g, 6.5 mmol) and 1,4-bis(2-tosyloxyethoxy)benzene **40** (1.500 g, 2.9 mmol). The reaction mixture was refluxed overnight, cooled and the precipitate was washed with boiling water (80 mL) and boiling solution of HCL (1M, 80 mL). The white precipitate was collected (1.1004 g, 63%).

Fluorobenzophenone monomer – 6th attempt

In a 100 mL, round-bottomed flask equipped with a nitrogen inlet, a condenser and a nitrogen outlet, drying tube and a magnetic stirrer was placed a solution of K_2CO_3 (1.703 g, 12.4 mmol) in acetone/water mixture (6.5/3.5, 40 mL) followed by the addition of 4-fluoro-4'-hydroxybenzophenone **22** (2.602 g, 12.0 mmol) and 1,4-bis(2-tosyloxyethoxy)benzene **40** (1.500 g, 3.0 mmol). The reaction mixture was refluxed for 66 h, cooled and poured into water (50 mL). The precipitate was filtered and slurried with hot methanol (20 mL). Hot filtration gave a white precipitate (1.431 g, 80%).

Fluorobenzophenone monomer – 7th attempt

In a 100 mL, round-bottomed flask equipped with a condenser, drying tube and a magnetic stirrer was placed a solution of KOH (1.680 g, 30.0 mmol) in EtOH (50 mL) followed by the addition of 4-fluoro-4'-hydroxybenzophenone **22** (3.240 g, 15.0 mmol) and 1,4-bis(2-tosyloxyethoxy)benzene **40** (1.501 g, 3.0 mmol). The reaction mixture was

refluxed for 66 h, cooled and poured into 400 mL of water. The precipitate was filtered and washed with hot methanol. The bright-yellow precipitate was collected by filtration (0.275g, 15%).

Fluorobenzophenone monomer – 8th attempt

In a 50 mL, round-bottomed flask equipped with a condenser, drying tube and a magnetic stirrer was placed a solution of KOH (0.770 g, 13.8 mmol) in NMP (20 mL) followed by the addition of 4-fluoro-4'-hydroxybenzophenone **22** (3.000 g, 46 mmol) and 1,4-bis(2-bromoethoxy)benzene **48** (1.350 g, 13.8 mol). The reaction mixture was stirred for 5 h at 90°, cooled and poured into 100 mL of water and stirred overnight. The product was filtered and dried to yield a pink-white precipitate (2.523 g, 92%).

Fluorobenzophenone monomer – 9th attempt

In a 50 mL, round-bottomed flask equipped with a condenser, drying tube and a magnetic stirrer was placed a solution of 4-fluoro-4'-hydroxybenzophenone **22** (0.700 g, 3.2 mmol) and KI (0.220 g, 0.13 mmol) in acetonitrile (26 mL) followed by the addition of K_2CO_3 (1.000 g, 7.23 mmol) and 1,4-bis(2-bromoethoxy)benzene **48** (0.501 g, 1.5 mmol). The reaction mixture was refluxed overnight, cooled and filtered. The precipitate was collected in the form of a white powder (0.645 g, 72%).

4-(2-hydroxyethoxy)-4'-fluorobenzophenone, 50

In a 50 mL, round-bottomed flask equipped with a nitrogen inlet, condenser, a nitrogen outlet and magnetic stirrer was placed 4-fluoro-4'-hydroxybenzophenone **22** (5.000 g, 23.0 mol), 2-chloroethanol (4.650 g, 57.7 mmol), sodium iodide (0.700 g, 4.6 mmol) and potassium carbonate (6.400 g, 46.3 mmol) and N,N-dimethylformamide (20 mL). The reaction mixture was heated at 95° and stirred under a nitrogen atmosphere for

4 h at which time additional 2-chloroethanol (1.500 g, 18.6 mol) and sodium iodide (0.250 g, 1.6 mmol) were added to the mixture. After an additional 14 h at 95°, the reaction mixture was quenched into NaOH solution (200 mL) with vigorous stirring. The solid was filtered and a white precipitate was collected (5.485 g, 91%): ^{1}H NMR ($CDCl_3$, δ) 4.03 (t, 2H, CH_2), 4.19 (t, 2H, CH_2), 7.01 (d, 2H, Ar), 7.16 (t, 2H, Ar), 7.80 (m, 4H, Ar).

4-(2-bromoethoxy)-4'-fluorobenzophenone, 52

A solution of triphenylphosphine (2.270 g, 8.6 mmol) and 4-(2-hydroxyethoxy)-4'-fluorobenzophenone **50** (2.250 g, 8.6 mmol) in dry acetonitrile (30 mL) was prepared in a 100 mL, round-bottomed flask equipped with nitrogen inlet, nitrogen outlet, addition funnel and magnetic stirrer. Tetrabromomethane (2.860 g, 8.6 mmol) was added portionwise under vigorous stirring. The mixture was stirred at room temperature for 4 h. The solvent was removed under vacuum and the remaining solid was dissolved in methanol (15 mL) and cooled to re-precipitate. White-yellow crystals were collected (1.275 g, 45%): mp. 77° - 80° C; ^{1}H NMR ($CDCl_3$, δ) 3.69 (t, 2H, CH_2), 4.40 (t, 2H, CH_2), 7.01 (d, 2H, Ar), 7.17 (t, 2H, Ar), 7.81 (m, 4H, Ar).

General 1,4-bis(2-tosyloxyethoxy)benzene/Bisphenol Polymerization Procedure

The polymerization was carried out in a 25 mL, three-necked round-bottomed flask equipped with a mechanical stirrer, a nitrogen inlet and a condenser with a nitrogen outlet. The calculated molar quantities of ditosylate **40** (1.000 g, 1.973 mmol) and the appropriate bisphenol (1.973 mmol) were dissolved with potassium hydroxide in a solution of dioxane and water (5:4 ratio). The reaction mixture was refluxed for 24 h.

After cooling, the mixture was filtered and the precipitate was washed with boiling water and boiling HCL (100 mL, 1 M).

Polymer 1, 52a

The bisphenol used in the polymerization was bisphenol A. A white powder was obtained in 76% yield: IR (KBr, cm^{-1}) 3421 (OH) 3042 (aromatic CH), 2963 (aliphatic CH), 1225, 1069 (C-O-C). Anal. Calcd. for $C_{25}H_{28}O_5$: C, 73.51%; H, 6.91%. Found: C, 72.75%; H, 6.62%.

Polymer 2, 52b

The bisphenol used in the polymerization was bisphenol AF. A white powder was obtained in 63% yield: IR (KBr, cm^{-1}) 3447 (OH), 3051 (aromatic CH), 2920 (aliphatic CH), 1255, 1069(C-O-C). Anal. Calcd. for $C_{25}H_{22}F_6O_5$: C, 58.14%; H, 4.29%. Found: C, 58.87%; H, 4.44%.

Polymer 3, 52c

The bisphenol used in the polymerization was bis(4-hydroxyphenyl)-diphenylmethane. A white powder was obtained in 73% yield: IR (KBr, cm^{-1}) 3446 (OH), 3052 (aromatic CH), 2923 (aliphatic CH), 1225, 1069 (C-O-C). Anal. Calcd for $C_{35}H_{32}O_5$: C, 78.92%; H, 6.06%. Found: C, 76.88%; H, 5.88%.

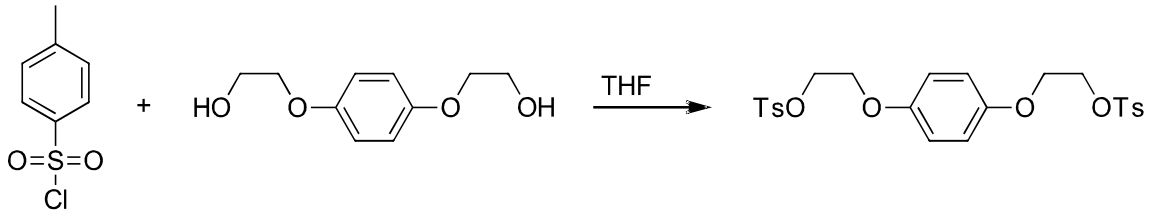
Polymer 4, 52d

The bisphenol used in the polymerization was 9,9-(4-hydroxyphenyl)fluorene. A white powder was obtained in 91 % yield: IR (KBr, cm^{-1}) 3449 (OH), 3036 (aromatic CH), 2920 (aliphatic CH), 1223, 1068 (C-O-C). Anal. Calcd for $C_{35}H_{30}O_5$: C, 79.22%; H, 5.70%. Found: C, 77.11%; H, 5.76%.

RESULTS AND DISCUSSION

1,4-bis (tosylethoxy) benzene, 40

The ditosylate that was used for monomer synthesis was prepared by tosylation of 1,4-bis(2-hydroxyethoxy)benzene **47** with p-toluenesulphonyl chloride **46** in THF. The ditosylate was characterized by ^{1}H NMR spectroscopy.



46 **47** **40**

The ^{1}H NMR spectrum of **40** exhibited unique absorptions in the aromatic region specific for hydrogen in a tosyl group. Doublet absorptions at 7.35 δ and 7.83 δ are associated with the protons on the aromatic ring of the tosylate group. A large singlet absorption at 6.71 δ corresponds to the protons in the symmetrical para-substituted aromatic ring derived from the diol. In the aliphatic region, the ^{1}H NMR confirmed the presence of alkyl chains. Triplet absorptions at 4.10 δ and 4.35 δ integrated to 4 protons each. A sharp singlet absorption located in the aliphatic region at 2.47 δ corresponds to the methyl substituents in the tosyl groups.

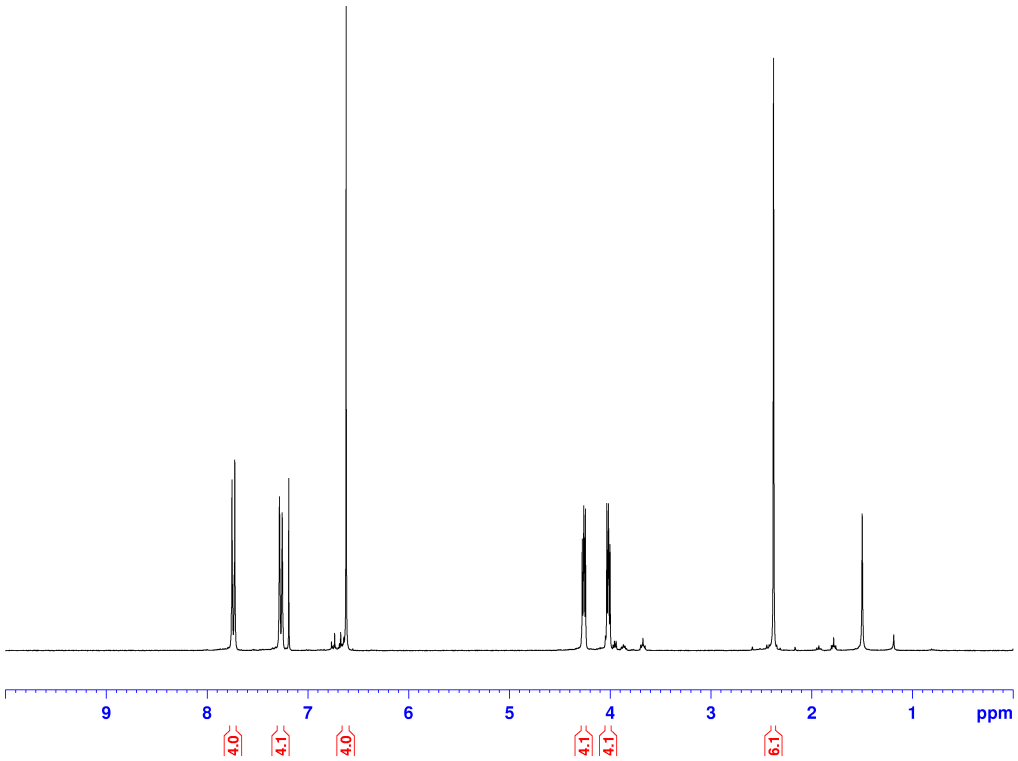
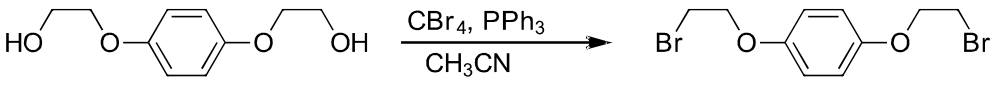


Figure 1. ^{1}H NMR spectrum of ditosylate **40.**

1,4-bis(bromoethoxy)benzene, 48

An alternative starting material for fluorobenzophenone monomer synthesis was synthesized by the conversion of an alcohol to an alkyl bromide by the Appel reaction. The reaction of 1,4-bis(2-hydroxyethoxy)benzene **47** with tetrabromomethane in acetonitrile in the presence of triphenylphosphine yielded 1,4-bis(bromoethoxy)benzene, **48**.



47 **48**

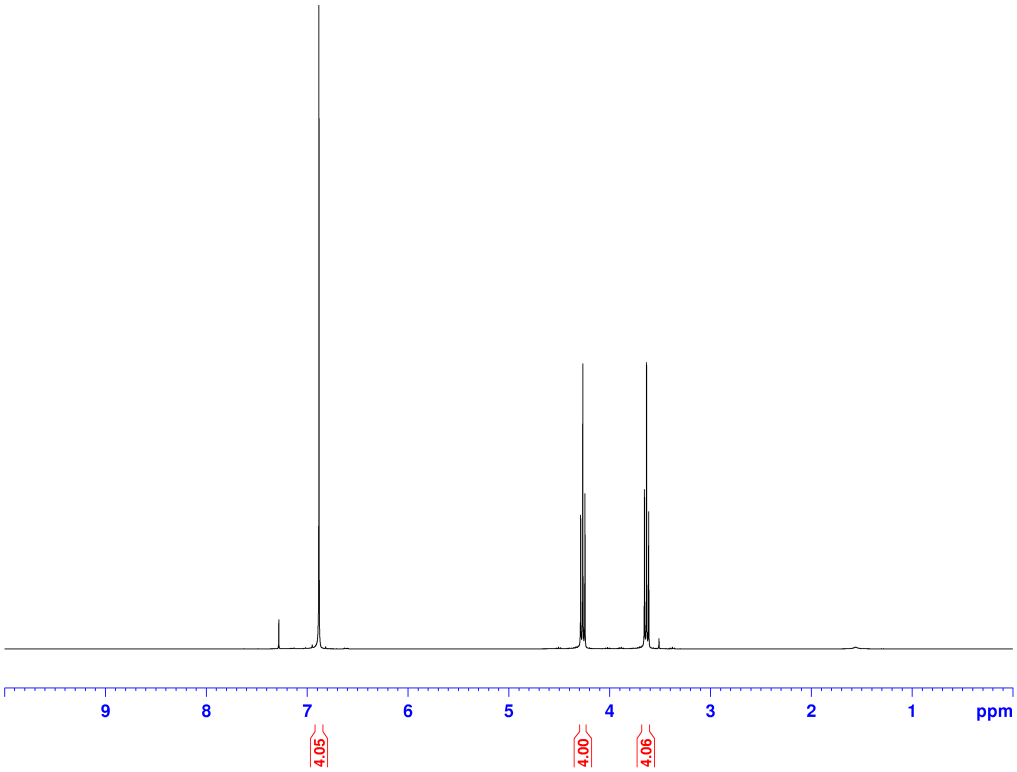
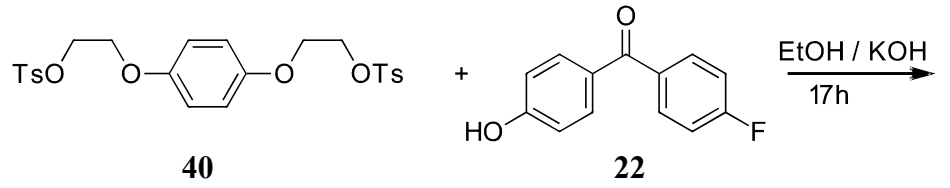


Figure 2. ^{1}H NMR spectrum of 1,4-bis(bromoethoxy)benzene **48.**

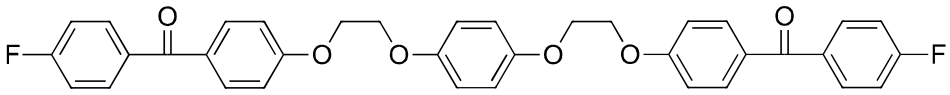
The ^{1}H NMR spectrum of the 1,4-bis(bromoethoxy)benzene, **48** (**Figure 2**) gave an overall integration of the aromatic region versus the aliphatic region being 4:8 as expected. The aromatic region showed a sharp absorption singlet at 6.88 δ associated with the hydrogens located on the symmetrical *para*-substituted aromatic ring, while the aliphatic region contained two triplets at 4.26 δ and 3.63 δ representing the protons in the alkyl chains.

Fluorobenzophenone Monomer, 49

The attempted synthesis of difluoro monomer **49** that could later be used in polymerizations was carried out, essentially in accordance to the previous work carried out with similar molecules by Patel, Patel and McGinty, as previously noted.



40 **22**



49

The product is expected to be a symmetrical molecule with a para-substituted aromatic ring in the middle of the structure. This should, in the ^{1}H NMR spectrum of **49,** give rise to a singlet absorption in the aromatic region similar to that observed in **Figure 1** and **2** for the ditosylate **40** and the dibromo compound **48**. The integration of aromatic and aliphatic regions should give a ratio of 20:8. A pair of absorption triplets in the aliphatic region representing aliphatic chains located on both sides of the middle ring should also be present. The aromatic region should also contain absorption peaks for the other 16 protons located in the fluorobenzophenone end groups (**Figure 3**). Theoretically, protons assigned **a** should have HH *ortho* coupling and HF *ortho* coupling and give a multiplicity of three (assuming the J values are identical). Proton absorptions assigned as **b** would be present as a pair of doublets. The protons assigned **c** and **d** would give absorption doublets as expected.

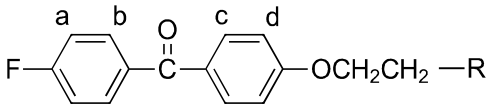


Figure 3. Fluorobenzophenone monomer end group with marked proton sets.

In the attempt to synthesize the fluorobenzophenone monomer **49**, different solvent systems were used with different reactant ratios or the reaction was run for a

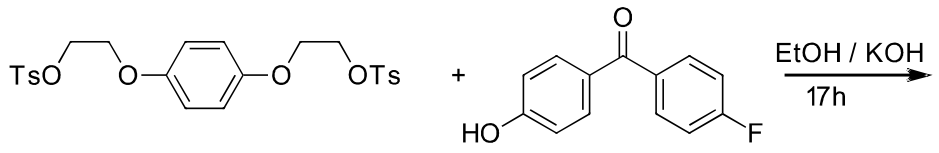
longer amount of time. **Table 1** shows a series of reaction conditions including the reaction conditions described previously.

Table 1. Reaction conditions used in the synthesis of bis(fluorobenzophenone) **49.**

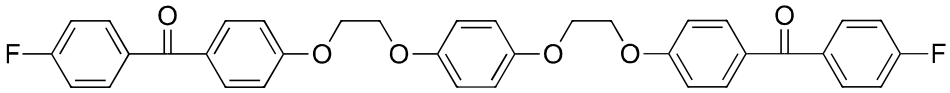
Attempt #	Solvent	Base	Rxn time	Reactants ratio
1.	EtOH	KOH	24h	1:2
2.	EtOH	KOH	24h	1:2
3.	NMP	K_2CO_3	6h	1:2
4.	H_2O/Acetone	K_2CO_3	66h	1:2
5.	H_2O/Dioxane	NaOH	24h	1:2
6.	H_2O/Acetone	K_2CO_3	66h	1:4
7.	EtOH	KOH	66h	1:5
8.	NMP	KOH	5h	1:2
9.	CH_3CN	K_2CO_3	12h	1:2

Fluorobenzophenone monomer - 1st attempt

The first attempt at monomer synthesis was performed by imitating previous methods and was done in EtOH in the presence of KOH as base for 17h.



40 **22**



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After 17 h, the product was collected, dried and analyzed. Due to insolubility of the product in DMSO-d_6, only a ^{1}H NMR spectrum could be obtained.

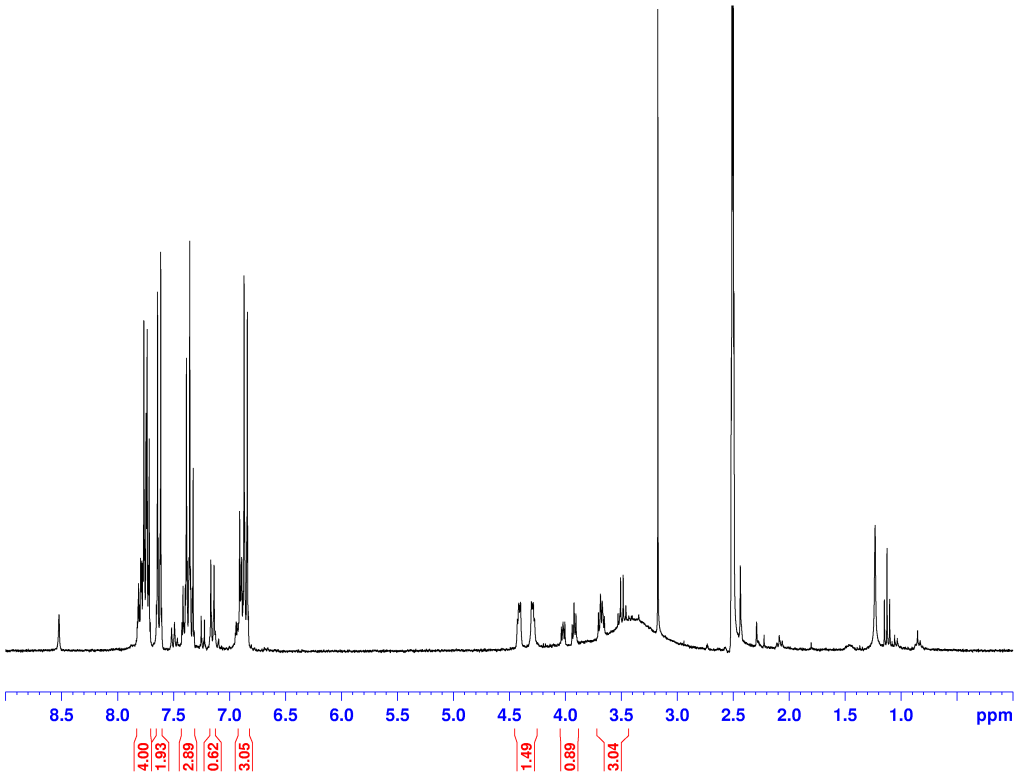


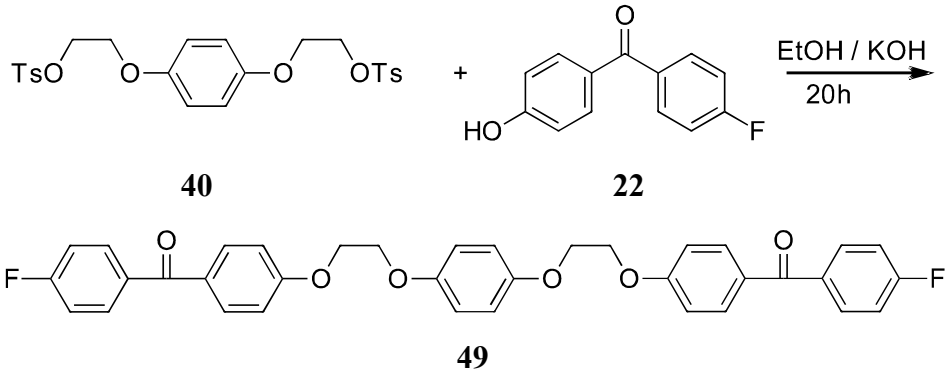
Figure 4. ^{1}H NMR spectrum of bis(fluorobenzophenone) monomer **49** - 1st attempt.

The ^{1}H NMR spectrum gave inconclusive results (**Figure 4**). The aromatic region as well as aliphatic region did not contain any sign of symmetry, i.e. the appearance of a singlet between 6.6 and 6.8 δ as observed for the ditosylate **40** and the dibromo compound **48**. Integration of aromatic versus aliphatic region (as well as could be done) gave a ratio of around 14:8. Although integration of the aliphatic region absorption peaks gives a total of 8 protons located in the alkyl chains of the molecule, a variety of multiplets can be found as opposed to the expected pair of triplet absorptions which should integrate to four protons each. This could mean that there is still starting material present and that the reaction was not complete. Next to the absorption peak at 2.5 δ, typical for the DMSO, there is a small absorption singlet that could be associated with the six protons of the methyl substituents in the tosyl groups since its location is the same as

the location of the sharp peak in the starting ditosylate **40**. It is a clear sign of the presence of the starting material in the product.

Fluorobenzophenone monomer – 2nd attempt

The synthesis was attempted additional two times with the same reaction conditions as the first attempt.



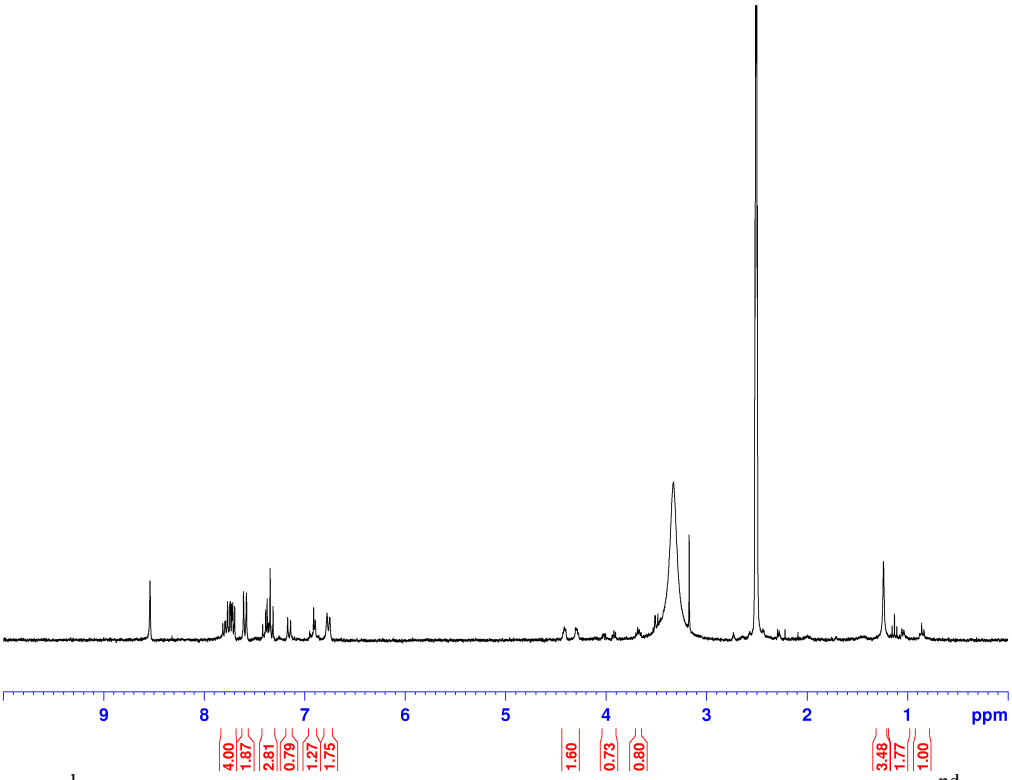


Figure 5. ^{1}H NMR spectrum of the bis(fluorobenzophenone) monomer **49** – 2nd attempt.

Again, the ^{1}H NMR spectrum (**Figure 5**) showed inconclusive results. Integration of the aromatic versus aliphatic regions gave a ratio of 12:3 confirming that the method

used in synthesis of previous fluorobenzophenone monomers was not successful for the desired monomer or at least did not give a pure product. As before, the absence of a singlet between 6.6 and 6.8 δ in the spectrum indicates the absence of the symmetrical *para*-substituted aromatic ring. The product from one of the repeated attempts was stirred in hot toluene and filtered. The ^{1}H NMR spectrum (**Figure 6**) of the filtered product showed absorption peaks characteristic of the starting material, ditosylate **40**, with matching integration of aromatic versus aliphatic region being 12:14.

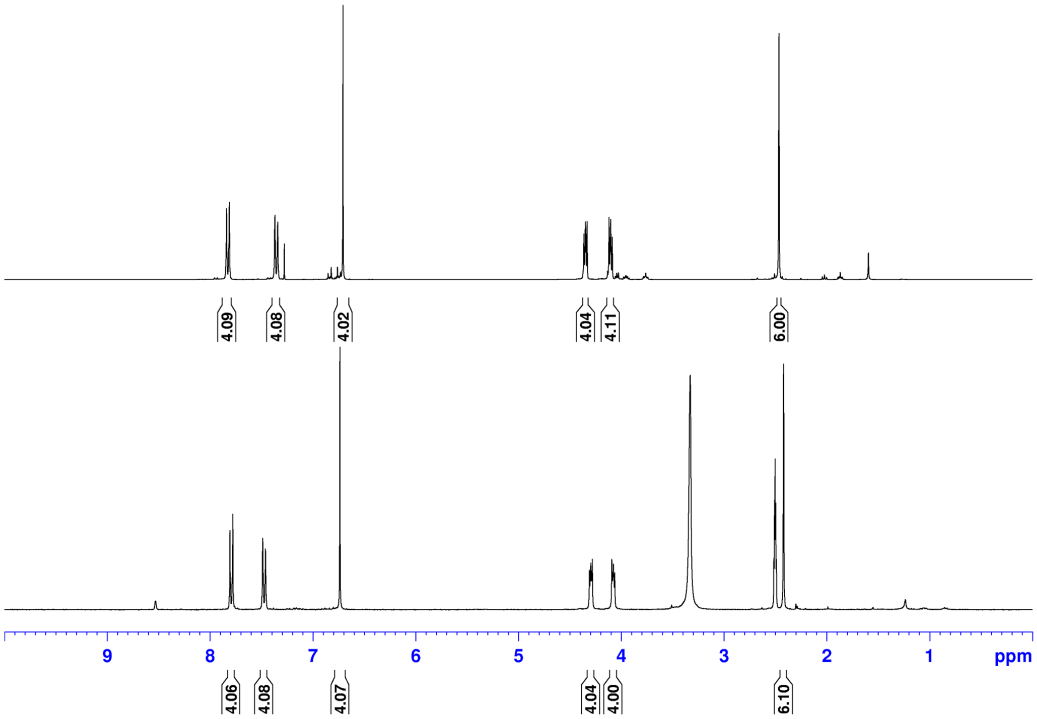
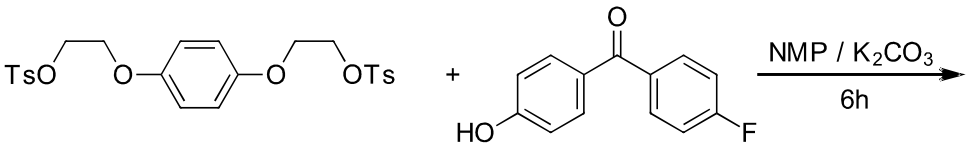


Figure 6. ^{1}H NMR spectrum of ditosylate **40** (top, $CDCl_3$) and the ^{1}H NMR spectrum of the product collected after recrystallization from toluene (bottom, DMSO-d_6).

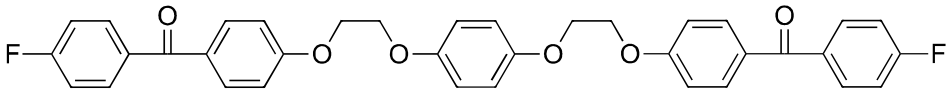
Fluorobenzophenone monomer – 3rd attempt

With the first two attempts being unsuccessful possibly due to EtOH not completely dissolving the ditosylate when it was added to the reaction mixture, a third attempt was

performed using K_2CO_3 as the base in NMP for 6 hours.



40 **22**



49

The ^{1}H NMR spectrum (**Figure 7**) obtained for the product collected after completion of the reaction gave inconclusive data with an integration ratio of approximately 10:7 between the aromatic and aliphatic absorption regions. Furthermore, lack of the sharp strong absorption peak (6.6 - 6.8 δ) in the aromatic region representing the protons located in the middle of the new molecule showed that the product of the reaction is not the desired symmetrical monomer **49.**

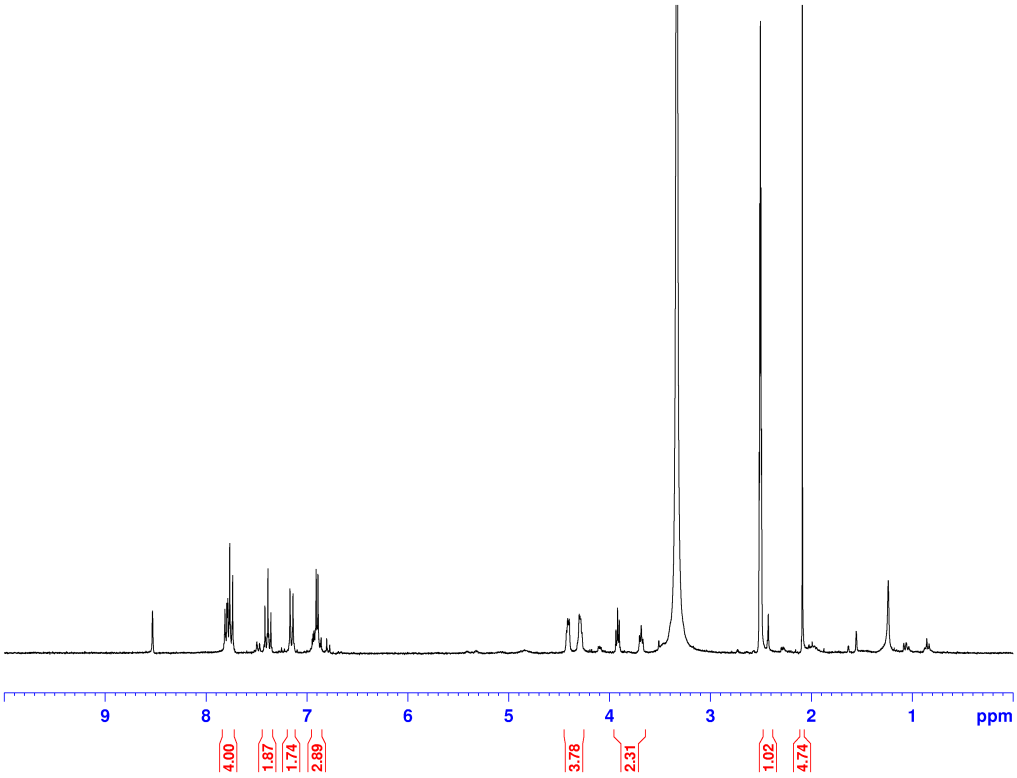
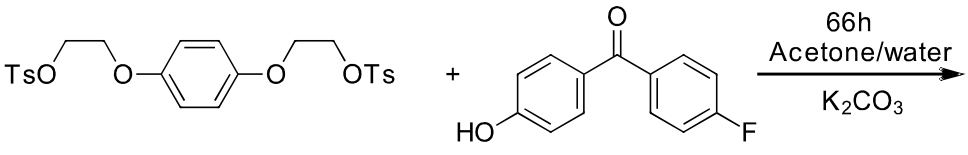


Figure 7. ^{1}H NMR spectrum of the bis(fluorobenzophenone) monomer **49** – 3rd attempt.

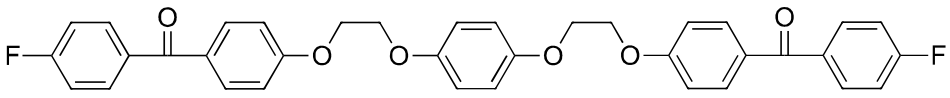
Similarly to the first attempt, there is a resemblance to the ^{1}H NMR spectrum of the starting material **40**, indicated by a weak, yet still present absorption peak at 2.4 δ. The integration of aliphatic region peaks also suggests some close similarity to the ditosylate **40** starting material. Other than the signal strength, there is very little difference in chemical shifts at 4.3 and 4.4 δ in the product from the third attempt of fluorobenzophenone monomer synthesis, compared to the proton absorptions of the ditosylate **40** (**Figure 1**). The other absorption peaks in the aliphatic region are similar to the expected absorption peaks for the expected bis(fluorobenzophenone) monomer. The peaks at 3.68 and 3.92 δ appear as two triplets integrated to a value close to two protons total. That value disagrees with the expected integration of total of eight protons for the aliphatic chains in the expected monomer.

Fluorobenzophenone monomer – 4th attempt

In the 4th attempt to synthesize the bis(fluorobenzophenone) monomer, a solvent mixture of water and acetone was used in the presence of K_2CO_3 as base over a period of 66h. The reaction was modeled on an example reported in 1966 by Jones and Mather.[12] They reported the reaction of ditosylate **40** with methyl p-hydroxybenzoate in a solvent system of water and acetone. The similarity of the structures of methyl



40 **22**



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p-hydroxybenzoate and 4-fluoro-4'-hydroxybenzophenone and the use of ditosylate **40** prompted the idea for the 4th attempt of bis(fluorobenzophenone) monomer synthesis.

The characterization of the product from the 4th attempt by ^{1}H NMR (**Figure 8**), showed different results compared to the previous attempts. The integration of the aromatic and aliphatic regions gave a ratio close to 11:8. Once again there were similarities with the ditosylate spectrum, with a strong absorption singlet at 2.4 δ most likely representing the protons of the methyl groups substituted on the rings of the tosylate end groups. The integration of the rest of the aliphatic region of the spectrum was far from expected most likely due to the presence of different products along with starting material in the sample. The pair of symmetrical multiplets found close to 4.5 δ in the

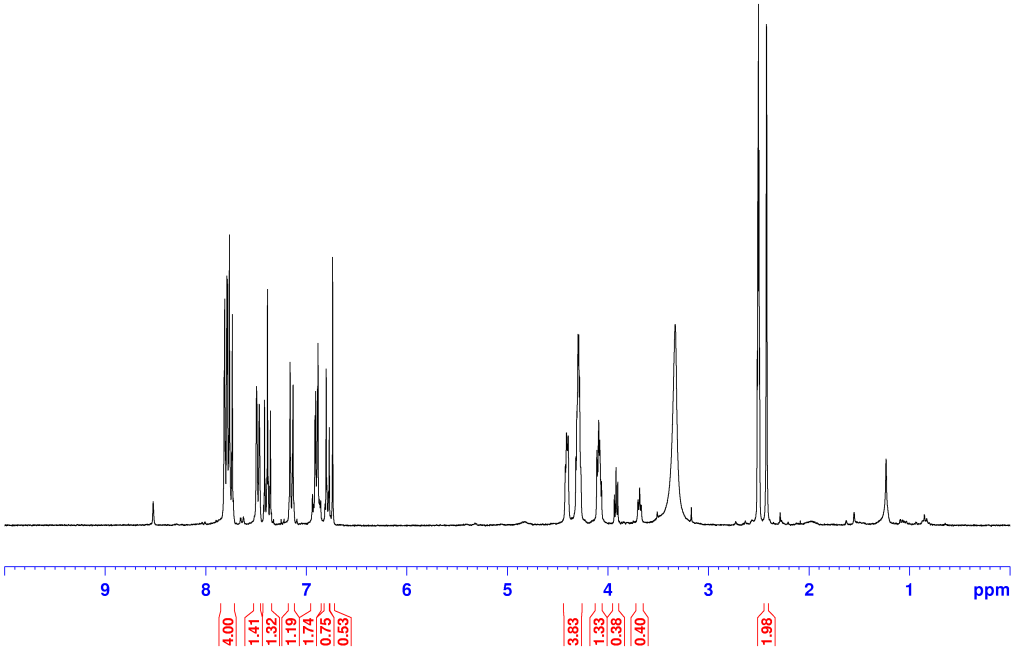


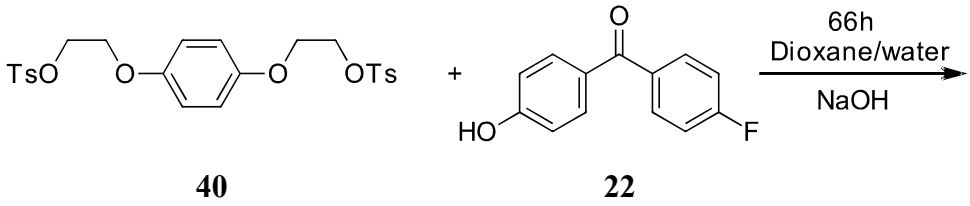
Figure 8. ^{1}H NMR spectrum of the bis(fluorobenzophenone) monomer **49** – 4th attempt.

previous attempts, presenting the protons from the alkyl chains of either new product or the ditosylate, was not symmetrical in the 4th attempt. Another difference from the previous spectra was a sharp absorption singlet in the aromatic region, although the

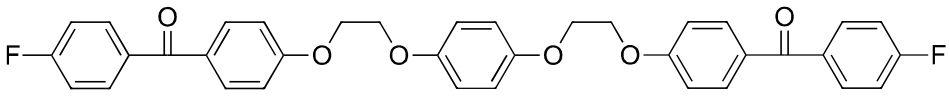
integration was inconclusive as to whether it can be associated with the symmetry of the molecule and there is a possibility it belonged to the starting material.

Fluorobenzophenone monomer – 5th attempt

Similar to the 4th attempt, the reaction model used for the 5th attempt was based on a patent by Reedr and Wallsgrove[11] that involved a reaction of ditosylate **40**. The reaction was performed in a solvent mixture of dioxane and water with sodium hydroxide as base.



40 **22**



49

The **i**ntegration of the aromatic and aliphatic region gave a ratio of 12:8 that is similar to the integration ratios for ditosylate **40**. However the absorption singlet at 2.4 δ, specific for methyl groups of the ditosylate, was not present. The aromatic region showed a multiplet around 7.7 δ that could represent the four protons residing *ortho* to the carbonyl of the fluorobenzophenone. The carbonyl function is a good electron-withdrawing group that makes it possible for those proton absorption peaks to be shifted downfield. On the other side of the benzophenone, fluorine, having an electron-donating effect, shifts the *ortho* proton signals more upfield, so the absorption triplet at 7.4 δ most likely represents those protons. The observed absorption data could indicate the formation of the half-product. If only one of the tosylate leaving groups underwent substitution, the product would not be symmetrical and that would correspond well with the given spectra since the aromatic absorption singlet, which would indicate the middle

ring as a center of a symmetrical molecule, is not present. On the other hand, it is also possible that both starting materials were present. The absorption doublet at 7.3 δ, next to the residual $CHCl_3$ singlet, showed almost no difference from the one in the spectra of the starting material, ditosylate **40**, potentially associated with the protons next to the methyl groups on ditosylate, **40.**

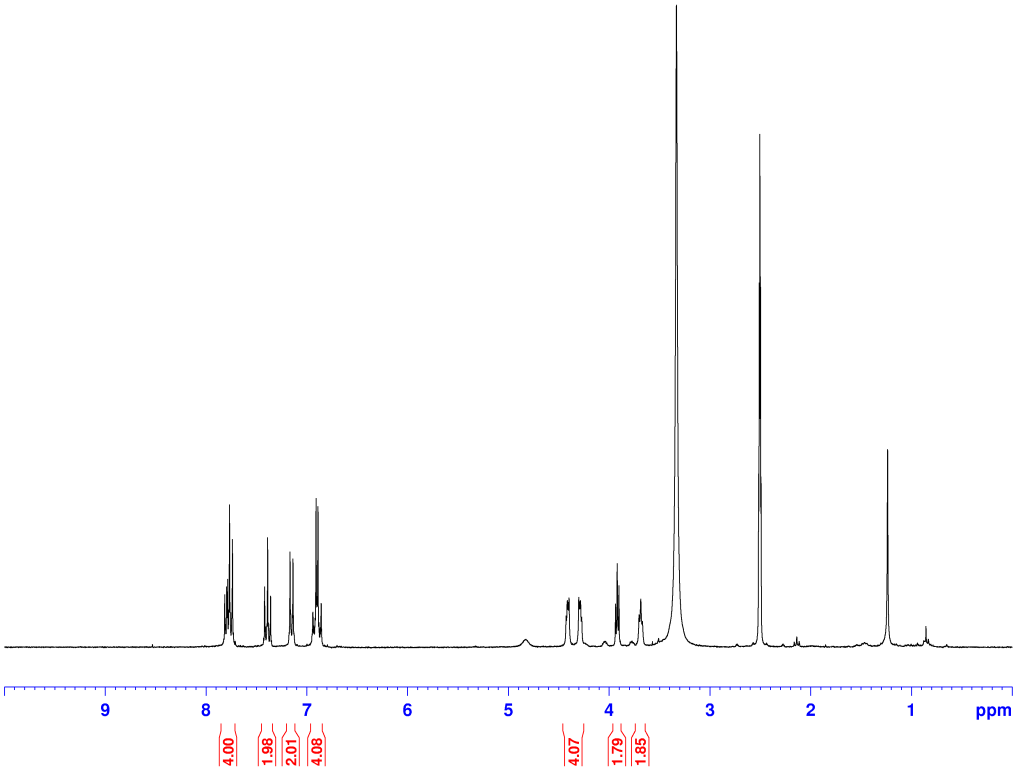
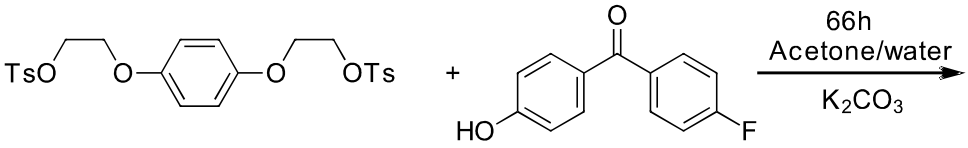


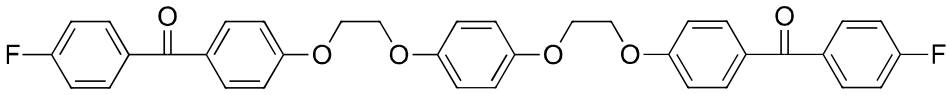
Figure 9. ^{1}H NMR spectrum of the bis(fluorobenzophenone) monomer **49** – 5th attempt.

Fluorobenzophenone monomer – 6th attempt

With the results of the 5th attempt being inconclusive and the ^{1}H NMR spectra of the other attempts suggesting that the half-product was forming, the reaction was repeated in a manner similar to the 4th attempt with the same solvent system and same base but with a different reactant ratio. Instead of a 1:2 ratio between the ditosylate and the 4-fluoro-4'-hydroxybenzophenone **22**, a ratio of 1:4 was used in order to promote the formation of the complete molecule instead of a half-product.



40 **22**



49

The results were again inconclusive. The ^{1}H NMR spectrum (**Figure 10**) showed the integration between aromatic and aliphatic absorption regions to be 11:7. The aromatic region did not contain an absorption peak that would indicate the presence of a symmetrical *para*-substituted aromatic structure. A multiplet at 7.7 δ, a triplet at 7.39 δ, a doublet 7.15 δ and a quartet at 6.9 δ showed very little difference from the previous two attempts. In the aliphatic region, a small absorption singlet at 2.4 δ, once again suggested the presence of the methyl groups of the ditosylate.

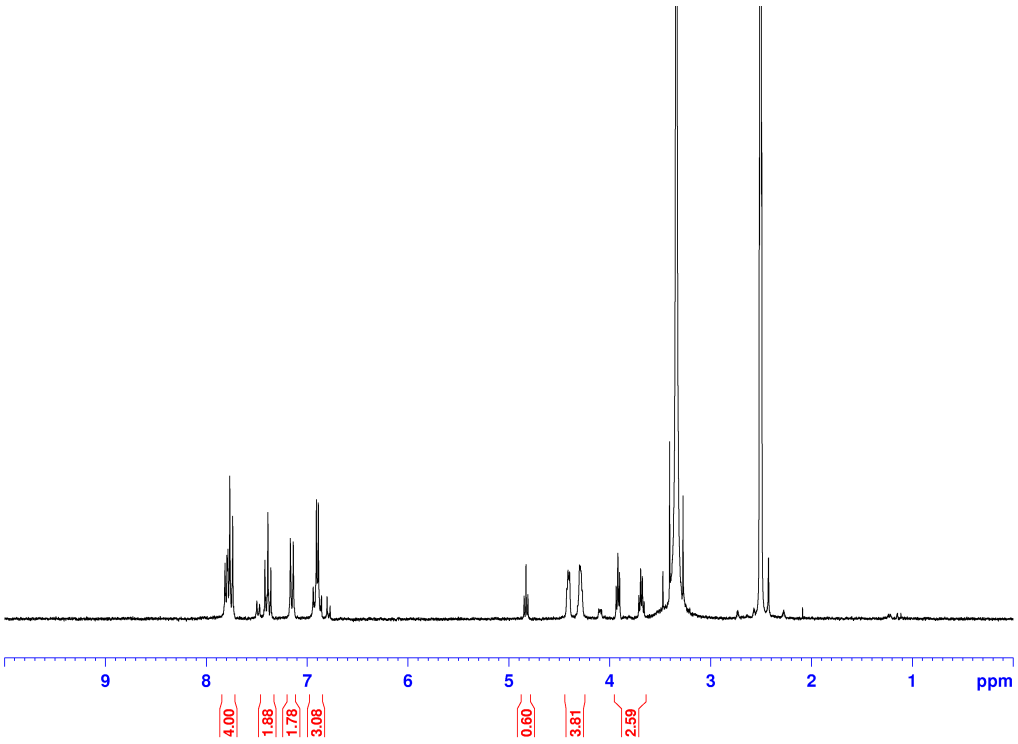
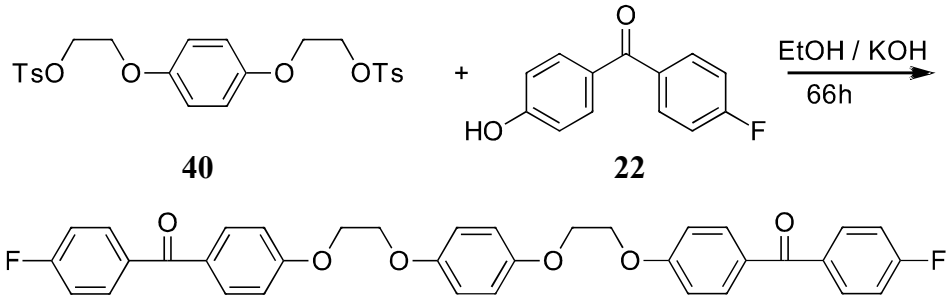


Figure 10. ^{1}H NMR spectrum of the bis(fluorobenzophenone) monomer **49** – 6th attempt.

Fluorobenzophenone monomer – 7th attempt

In the 7th attempt, the reaction was carried out in EtOH with KOH as base. The ratio of the reactants was increased to 5:1 (4-fluoro-4'-hydroxybenzophenone:ditosylate) and the reaction was refluxed for 66 hours.



40 **22**

49

The ^{1}H NMR spectrum of the product (**Figure 11**) showed results similar to the first two attempts. The aromatic region was integrated to a total of 12 protons, while aliphatic region integration gave a total of 13 protons. However, EtOH was not

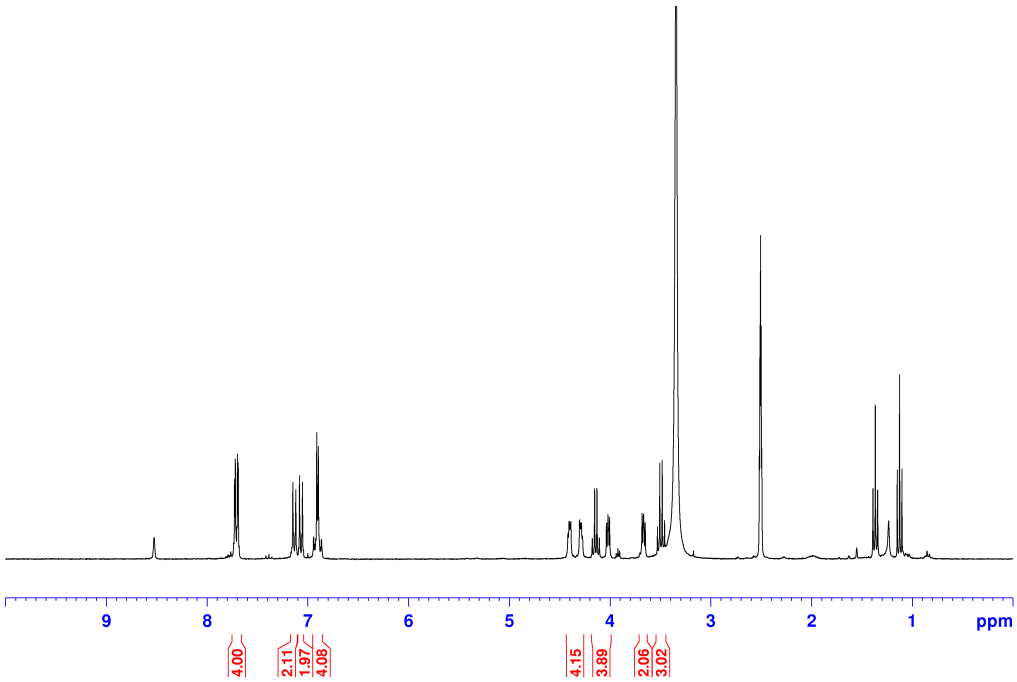


Figure 11. ^{1}H NMR spectrum of the bis(fluorobenzophenone) monomer **49** – 7th attempt.

completely removed from the product so the aliphatic region contained EtOH absorptions.

Fluorobenzophenone monomer – 8th attempt

The 8th attempt to synthesize the fluorobenzophenone monomer utilized a different starting material. Instead of 1,4-bis(2-tosylethoxy)benzene **40**, which was used in the previous 7 attempts, 1,4-bis(bromoethoxy)benzene **48** was used. The reaction was carried out in NMP with KOH as a base for 5 hours.

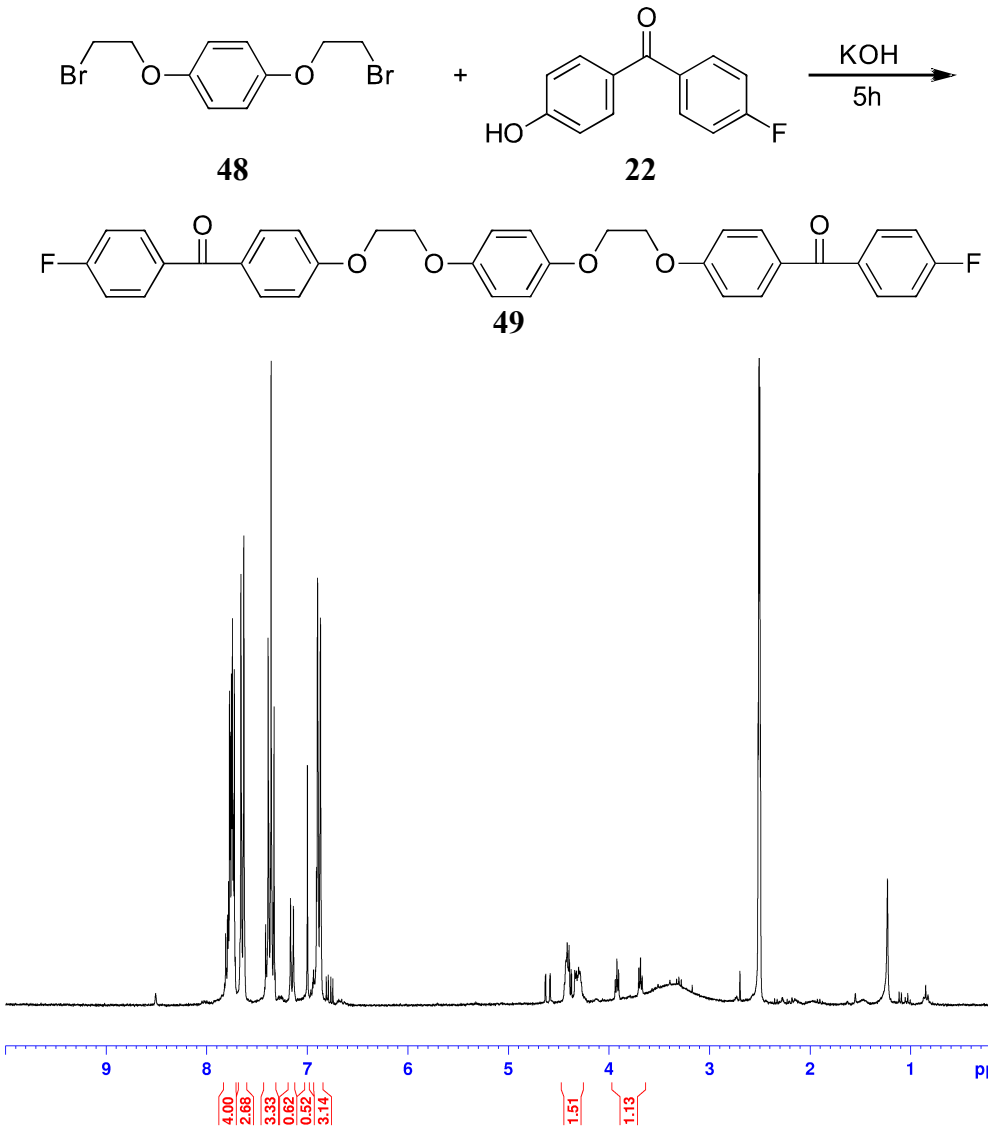
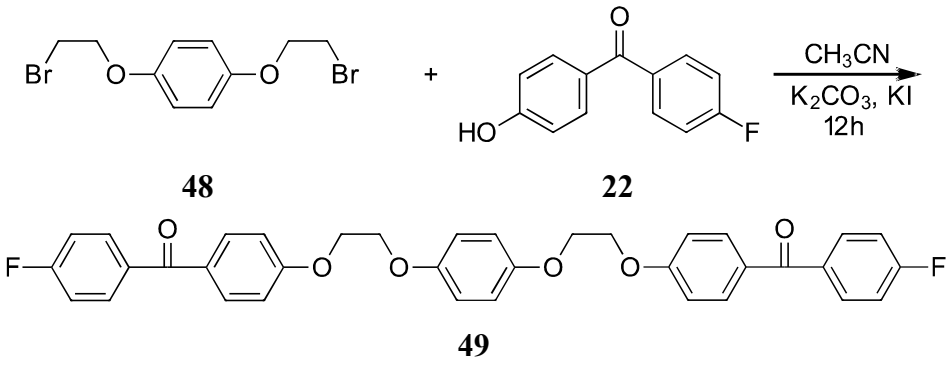


Figure 12. ^{1}H NMR spectrum of the bis(fluorobenzophenone) monomer **49** – 8th attempt

The ^{1}H NMR spectrum of **49** (**Figure 12**) showed similar results as for the previous attempts. Integration of aromatic and aliphatic region gave a ratio of 10:3. The aliphatic region showed absorption peaks specific for alkyl chains with low intensity. The absorption peak at 7.0 δ in the aromatic region indicates the presence of the starting 1,4-bis(2-tosylethoxy)benzene, **40,** due to its low intensity.

Fluorobenzophenone monomer – 9th attempt

The last attempt employed the same starting materials as used in the 8th attempt, 1,4-bis(bromoethoxy)benzene **48** and 4-fluoro-4'-hydroxybenzophenone **22**. The reaction was carried out in CH_3CN in the presence of the K_2CO_3 and KI overnight.



48 **22**

49

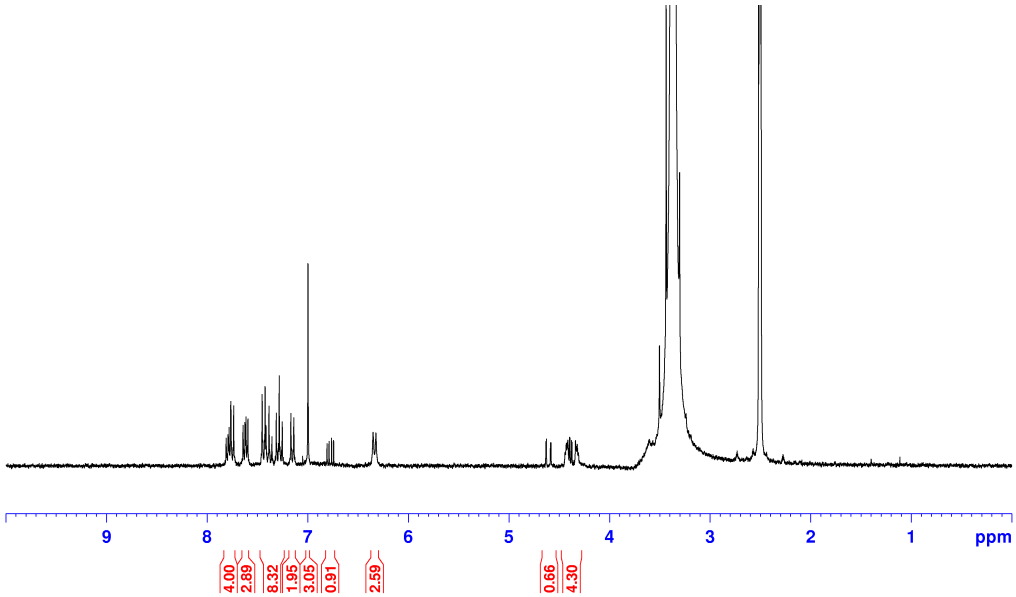


Figure 13. ^{1}H NMR spectrum of the bis(fluorobenzophenone) monomer **49** – 9th attempt.

The analysis of the ^{1}H NMR spectrum for **49** is similar to results obtained for the 8th attempt. The aliphatic region showed an absorption multiplet at 4.4 δ corresponding to the protons in the alkyl chain. The aromatic region gave a relative integration of 23 protons that probably indicates the presence of starting material.

Fluorobenzophenone Monomer Synthesis Conclusions

The synthesis of a bis(fluorobenzophenone) monomer using 1,4-bis(tosylethoxy)benzene or 1,4-bis(bromoethoxy)benzene with 4-fluoro-4'-hydroxybenzophenone was unsuccessful. Changing the solvent system, reaction time and/or reactant ratio did not improve the outcome of the reaction. One possible explanation is that the tosylate or bromo groups undergo substitution only at one tosylate location of the starting molecule, creating a "half" product containing only one 4-fluorobenzoylphenoxy group. Although it is inconclusive, the ^{1}H NNR data supports this theory. The ^{1}H NMR spectrum aromatic region did not contain the specific peak, a singlet, which would indicate the presence of the symmetrical *para*-substituted ring of **49**.

Another possibility is that the formation of the desired molecule is not possible due to steric effects in **40**. Alternately, the original aromatic ring in the ditosylate **40** could be creating a sort of π- π stacking effect with the rings of the fluorobenzophenone from the first substitution making the second substitution less likely (**Figure 14)**.

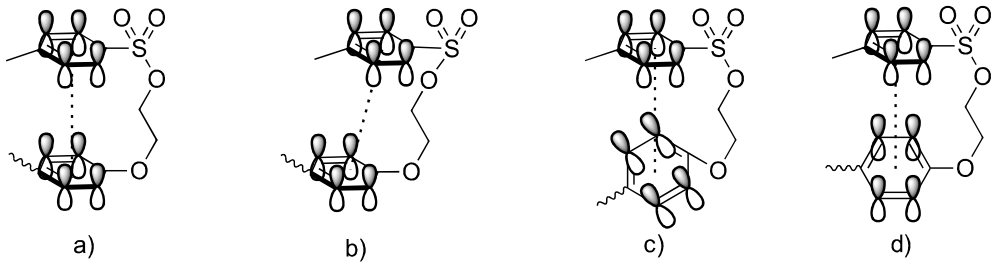


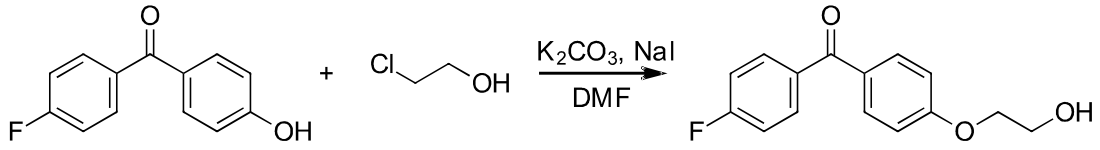
Figure 14. Possible π - π effect (**a**-parallel; **b**-parallel offset, **c**-T-shaped, **d**-Y-shaped)

A Different Approach to the Bis(fluorobenzophenone) Monomer

In the attempt to find an alternate approach to synthesizing a bis(fluorobenzophenone)monomer, the synthesis of an alternative hydroxyethoxy containing component, 4-(2-hydroxyethoxy)-4'-fluorobenzophenone was synthesized. Unlike the previous attempts of synthesis, the monomer could be created by synthesizing the end groups first and then assemble the monomer by reaction with hydroquinone.

4-(2-hydroxyethoxy)-4'-fluorobenzophenone, 50

The first part of the new approach was to synthesize 4-(2-hydroxyethoxy)-4'-fluorobenzophenone, **50.**[14] The reaction of 4-hydroxy-4'-fluorobenzophenone **22** and 2-chlorethanol, **51** was carried out in DMF in the presence of potassium carbonate and sodium iodide.



22 **51** **50**

The ^{1}H NMR spectrum (**Figure 15**) showed the expected absorptions. The integration of the aromatic and aliphatic region gave a proton ratio of 8:5. An absorption multiplet at 7.80 corresponds to the four protons located next to the carbonyl, while the other aromatic proton absorptions appear more upfield as a triplet at 7.16 δ and an absorption doublet at 7.01 δ. The aliphatic region exhibited a pair of triplet absorptions at

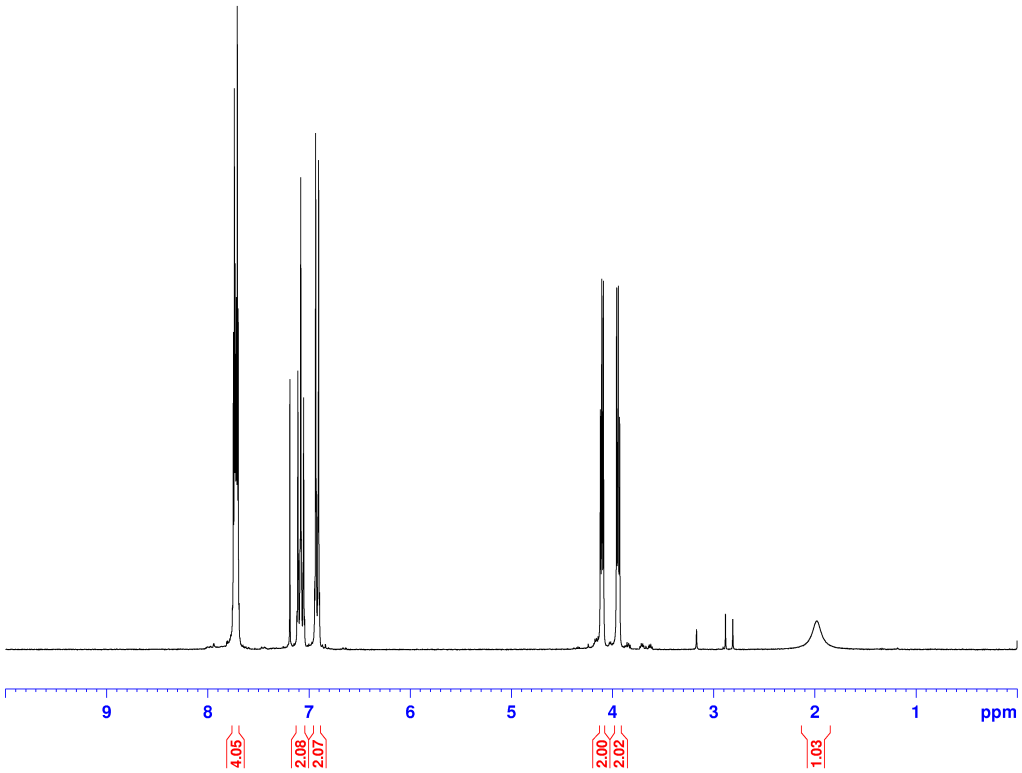


Figure 15. ^{1}H NMR spectrum of the 4-(2-hydroxyethoxy)-4'-fluorobenzophenone **50.**

4.19 δ and 4.03 δ indicative of the protons in the alkyl chain, while a broad absorption peak at 2.01 δ is associated with the proton of the OH group.

4-(2-bromoethoxy)-4'-fluorobenzophenone, 52

The second step in the new approach for the synthesis of the bis(fluorobenzophenone) monomer is converting the 4-(2-hydroxyethoxy)-4'-fluorobenzophenone **50** to an alkyl halide which would be prone to attack by the deprotonated form of hydroquinone.

The conversion of 4-(2-hydroxyethoxy)-4'-fluorobenzophenone, **50** to 4-(2-bromoethoxy)-4'-fluorobenzophenone, **52** was carried out in acetonitrile in the presence of triphenylphosphine and tetrabromomethane at room temperature. The byproduct of the reaction is triphenylphoshine oxide and can be difficult to remove. The product was

dissolved in methanol at room temperature and cooled to temperatures below 0° and filtered in order to successfully remove the byproduct.

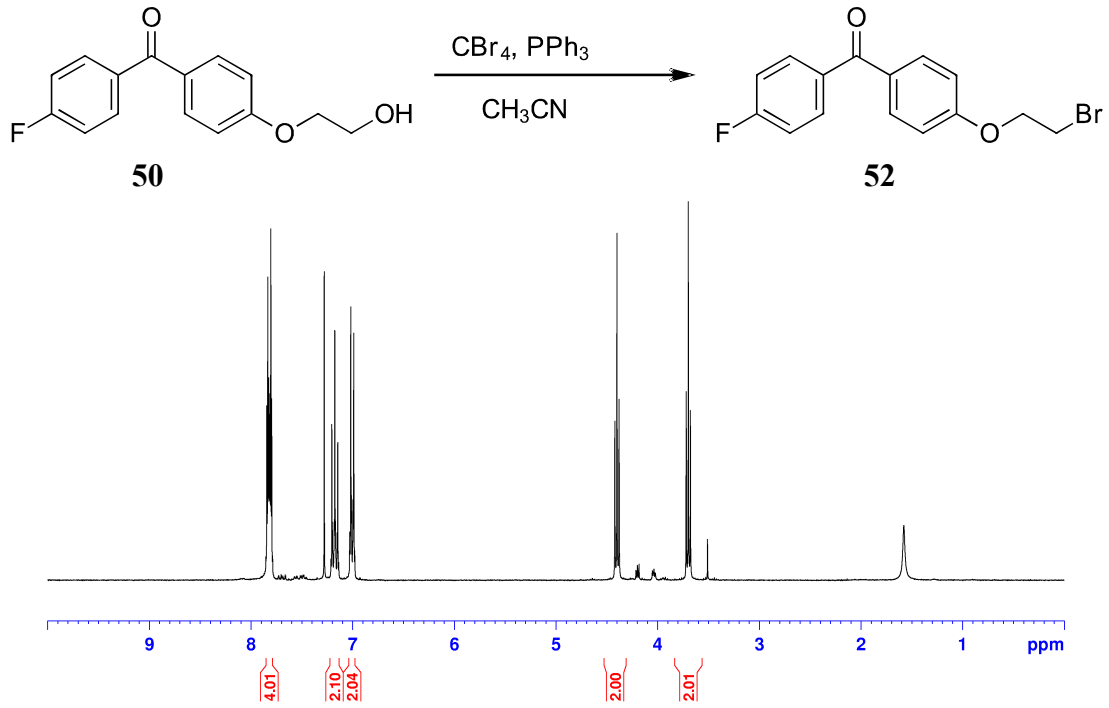


Figure 16. ^{1}H NMR spectrum of the 4-(2-bromoethoxy)-4'-fluorobenzophenone **52.**

The ^{1}H NMR spectrum (**Figure 16**) exhibited similar absorptions as the previous 4-(2-hydroxyethoxy)-4'-fluorobenzophenone, **50**. The aromatic region again showed an absorption multiplet at 7.81 δ associated with the four protons *ortho* to the carbonyl. A triplet absorption at 7.17 δ and a doublet absorption at 7.01 δ are associated with the remaining aromatic protons. A pair of triplet absorptions associated with the alkyl protons were found at 4.40 δ and 3.69 δ.

When compared (**Figure 17**) to the previous spectra of 4-(2-hydroxyethoxy)-4'-fluorobenzophenone, **50,** the aliphatic absorption peaks are more separated due to the replacement of the OH by a bromine atom at the end of the chain.

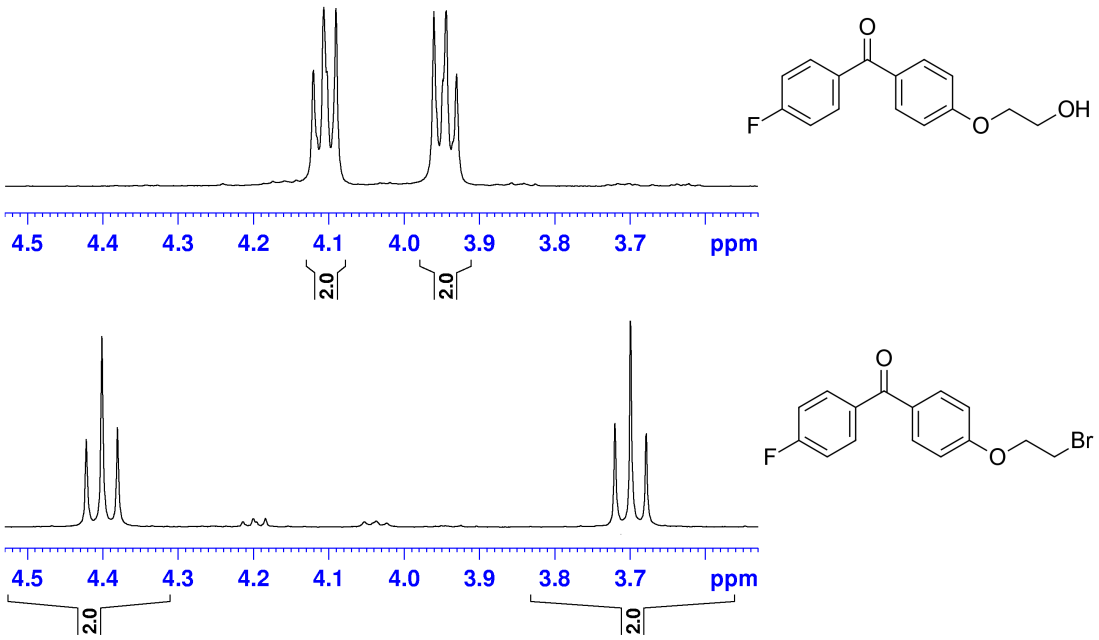
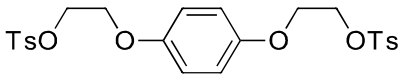


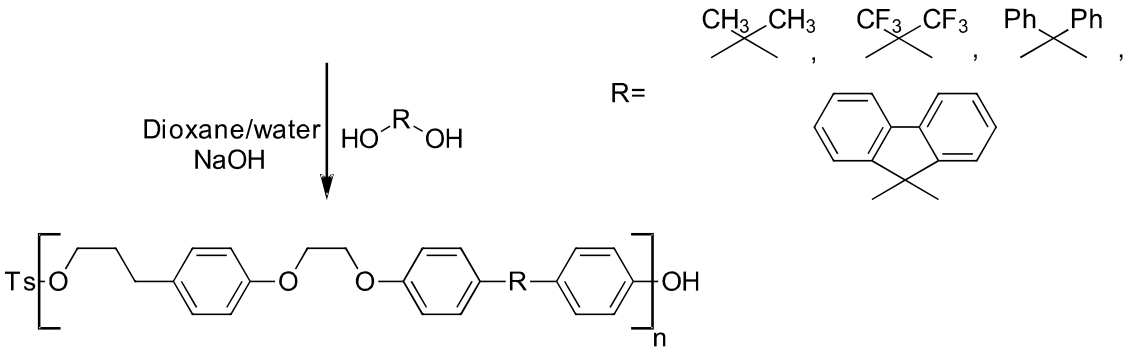
Figure 17. [1]H NMR Spectrum aliphatic regions of 4-(2-hydroxyethoxy)-4'-fluorobenzophenone **50** and 4-(2-bromoethoxy)-4'-fluorobenzophenone **52.**

Polymerization of Ditosylate 40

The polymerization of the ditosylate, **40** with the appropriate bisphenol was carried out in dioxane/water solvent mixture using sodium hydroxide as a base to yield the corresponding poly(aralkyl ether)s **52a-d**.



40



52a-d

Polymerization of ditosylate **40** with bisphenol-A, bisphenol-AF, bis(4-hydroxyphenyl)diphenylmethane and 9,9-bis(4-hydroxyphenyl)fluorene yielded the polymers **52a-d** as white powders. Thermal analysis (TGA, **Figures 22 and 23**) of polymers **52a-d** gave 5% weight loss temperatures of 338°, 350°, 365° and 377°, respectively.

The IR spectra of polymers **52a-d** (**Figures 18-21**) showed characteristic peaks for ether functions and terminal hydroxyl groups. The stretching absorptions of aryl alkyl ether linkages (C-O-C) were found at 1225 and 1069 cm^{-1} for the polymers **52a**-c, while polymer **52d** had peaks at 1223 and 1068 cm^{-1}.

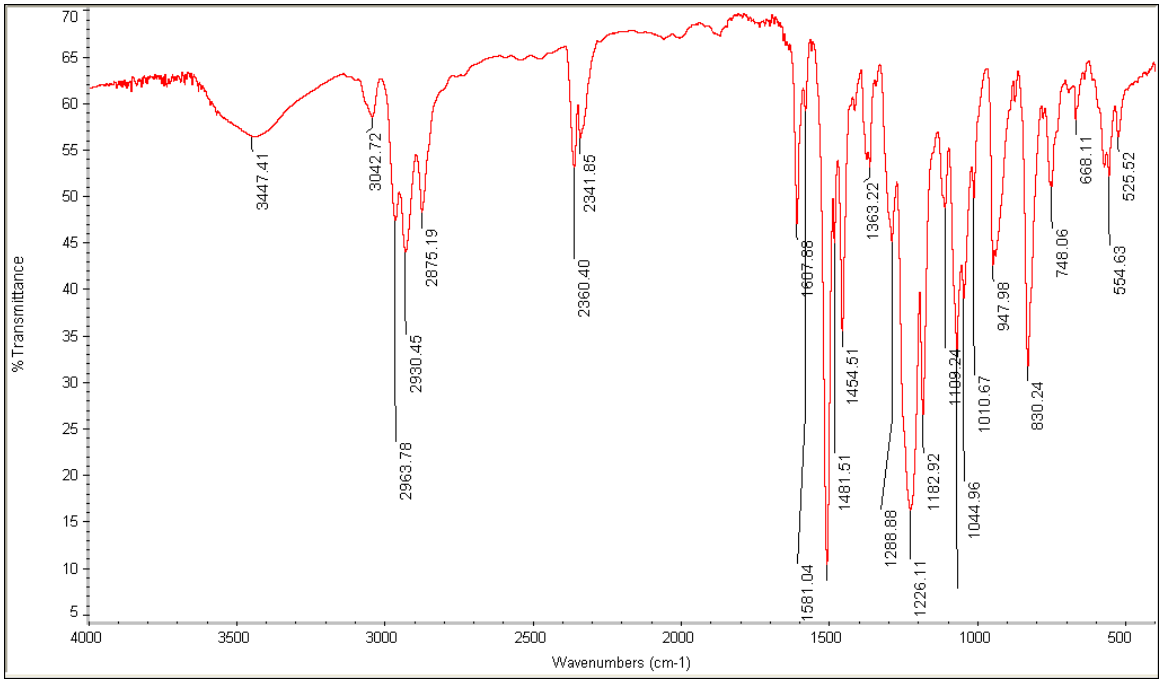


Figure 18. IR spectrum (KBr) of polymer **52a.**

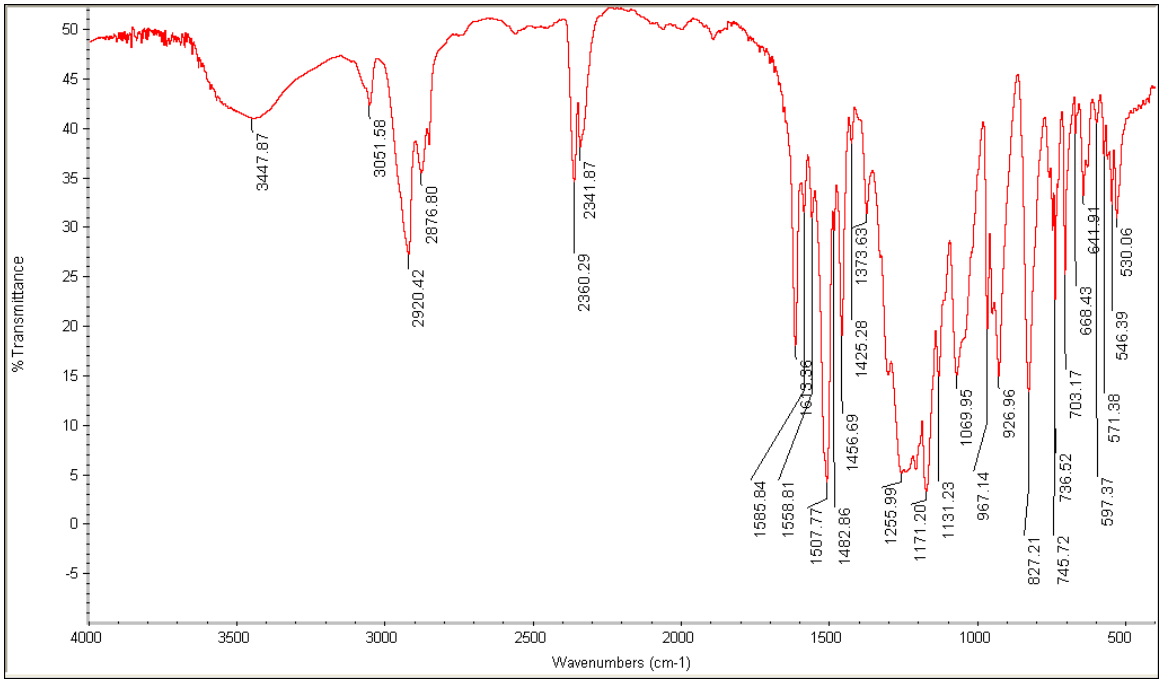


Figure 19. IR spectrum (KBr) of polymer **52b.**

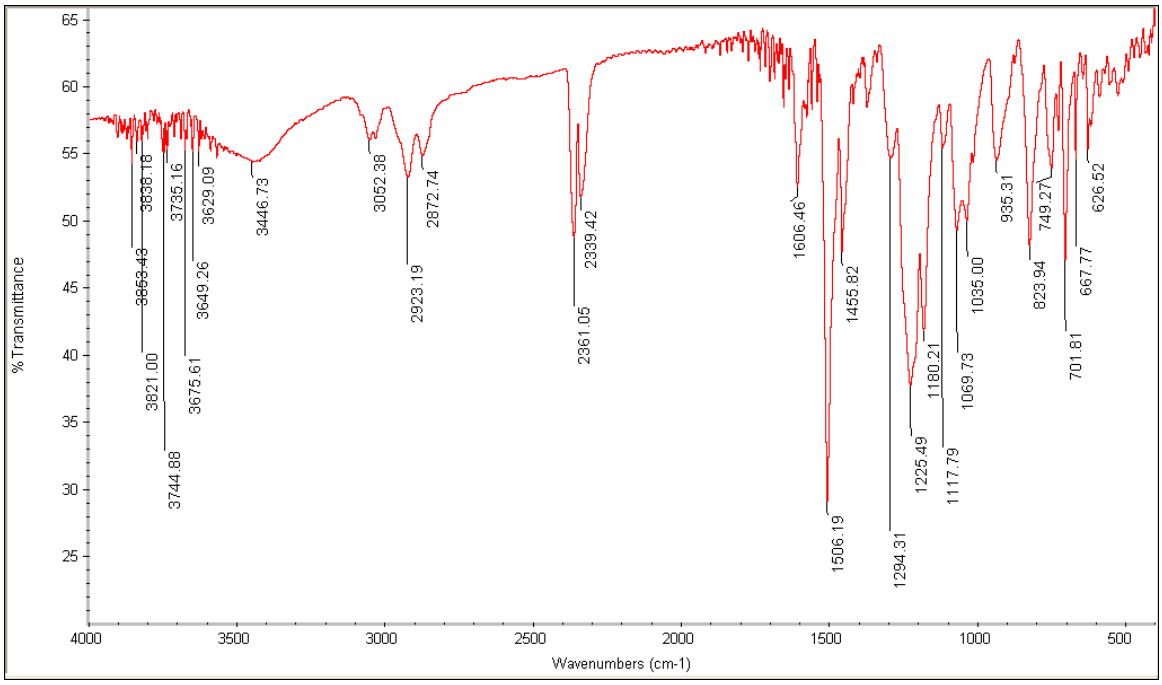


Figure 20. IR spectrum (KBr) of polymer **52c.**

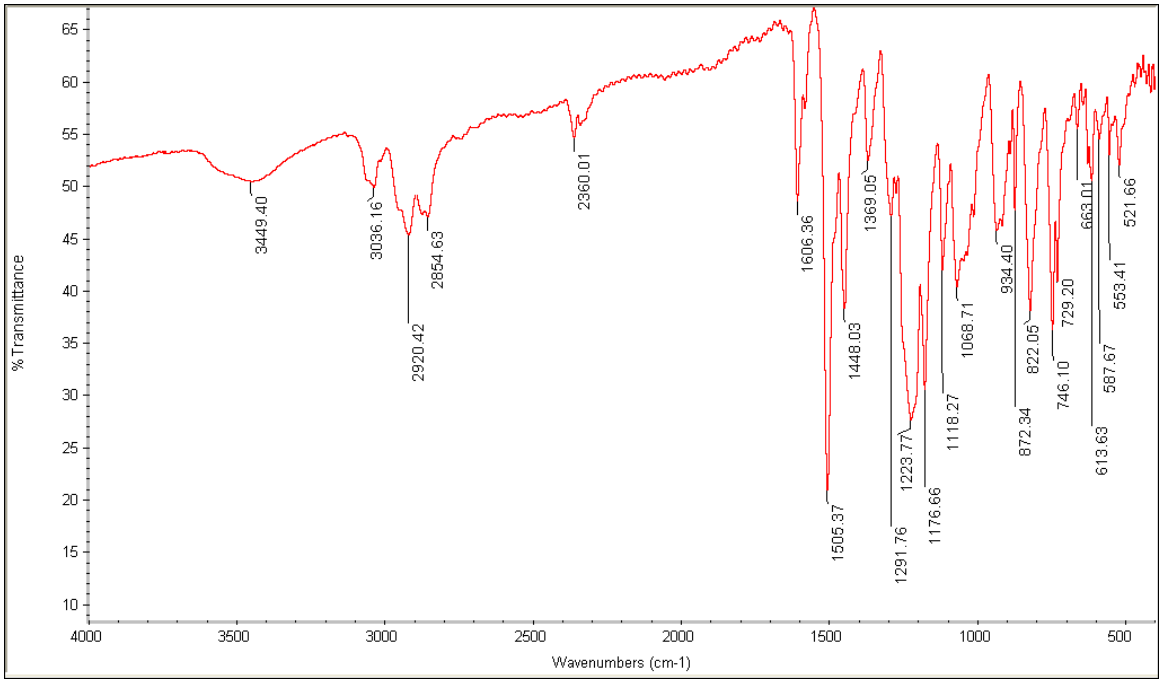


Figure 21. IR spectrum (KBr) of polymer **52d.**

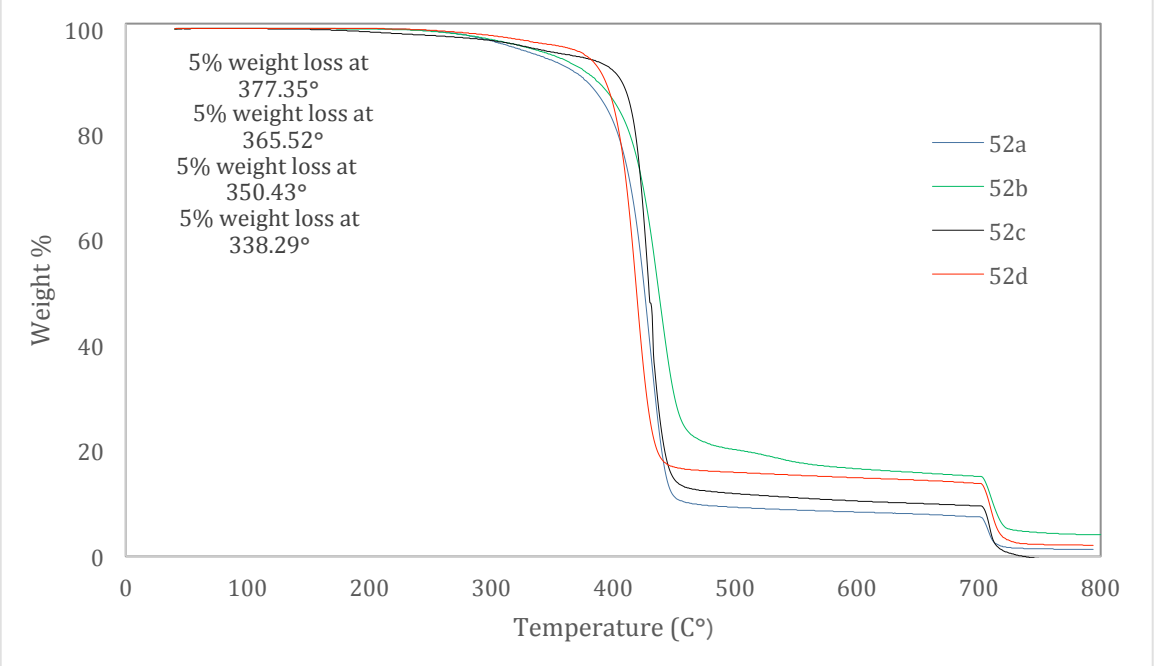


Figure 22. TGA of polymers **52a-d.**

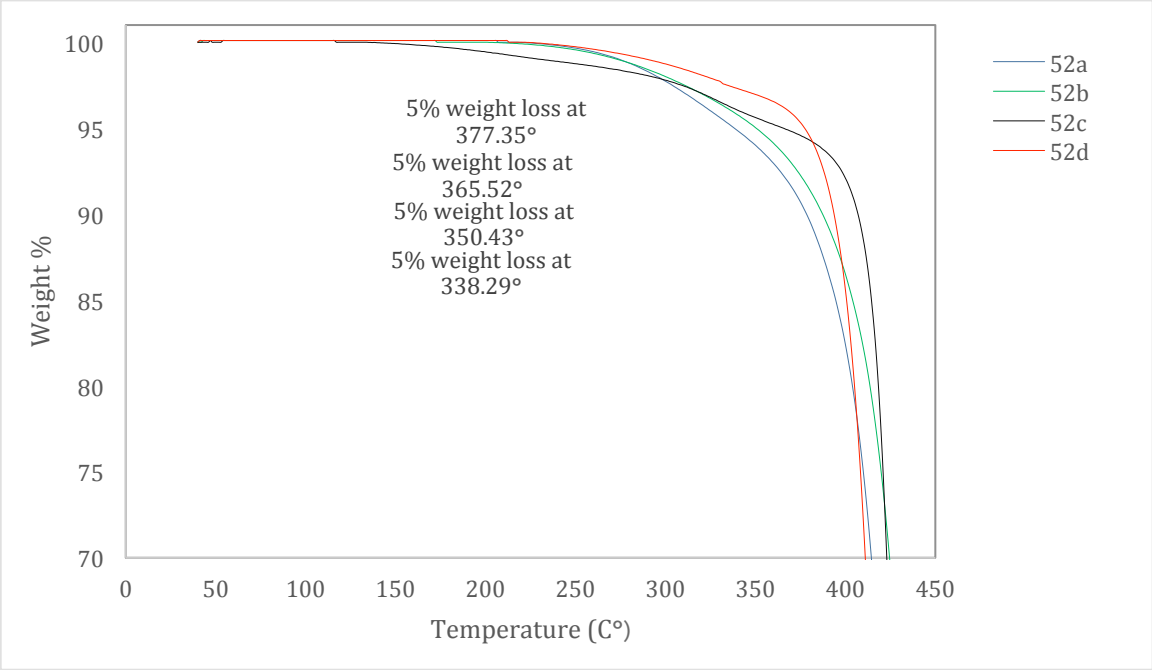


Figure 23. Expanded TGA spectrum of polymers **52a-d.**

The solubility of the polymers **52a-d** (**Table 2**) was investigated over a period of 24 hours by mixing 4 mg of the polymer with 1 mL of an appropriate solvent. All the polymers were at least partially soluble in most of the solvents.

Table 2. Solubility of polymers **52a-d**.

Solubility	52a	52b	52c	52d
m-Cresol	-	+	+	+
DCM	±	-	±	±
NMP	+	±	+	+
Tetrachloroethane	+	±	+	+
$CHCl_3$	-	-	±	-
THF	±	-	±	±
DMAC	±	±	±	-
DMSO	±	-	-	-
DMF	±	-	-	-
Acetone	±	-	-	-

(+ soluble; - not soluble; ± partially soluble)

Summary

Numerous attempts to synthesize a new bis(fluorobenzophenone) monomer, 1,4-bis (2-(4-(4-fluorobenzoyl)phenoxyethoxy)benzene **49**, were unsuccessful in spite of the use of a variety of conditions. Monosubstitution and elimination reactions may be important side reactions.

The polymerization of 1,4-bis(2-tosyloxyethoxy)benzene **40** with a series of bisphenols gave a series of poly(aralkyl ether)s. Although the molecular weights were not determined, the polymers showed good thermal stability in a nitrogen atmosphere. It appears that having larger aromatic units in the bisphenol can improve the thermal stability and solubility of the polymers.

Future Work

The synthesis of a bis(fluorobenzophenone) monomer using 4-(2-bromoethoxy)-4'-fluorobenzophenone **52** and hydroquinone needs to be further investigated.

Creating bis(fluorobenzophenone) monomers using alternate bis(hydroxyethoxy)aromatics should be investigated. The steric influence of the central aromatic unit could be investigated.

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VITAE

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